Manipulating and determining the electronic structure of carbon nanotubes

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Outline

Introduction

- What is carbon and its tubule structure
- Synthesis and geometrical structure of carbon nanotubes
- Electronic structure of carbon nanotubes

Bandgap modulation

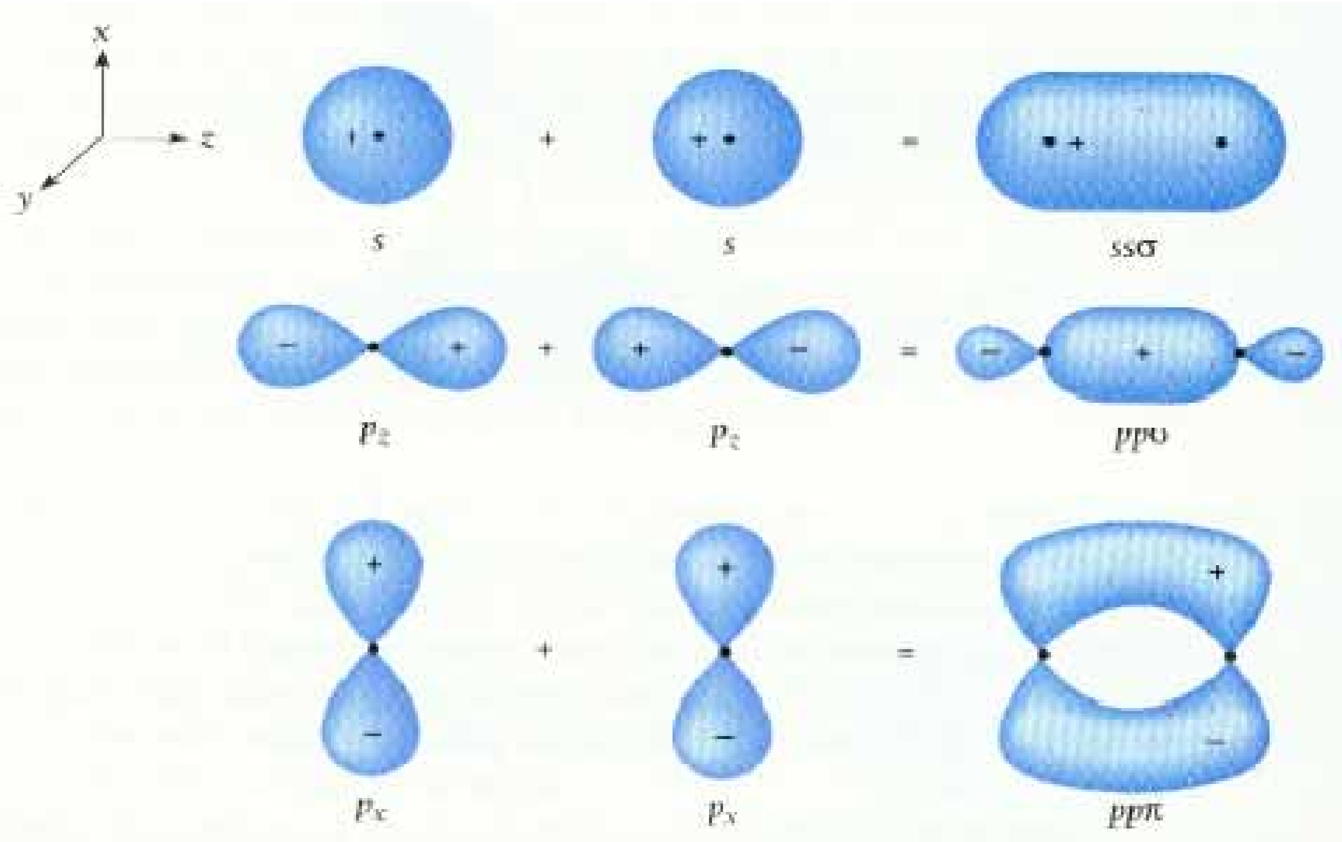
- Nanotube peapod
  - ★ Synthesis and device fabrication
  - ★ Temperature dependent conduction in metallic tubes
  - ★ Temperature dependent conduction in semiconducting tubes
- Nanotube T junction
  - ★ Chemical linking
  - ★ Reversible and irreversible modulation

Nanotube index assignment

Summary

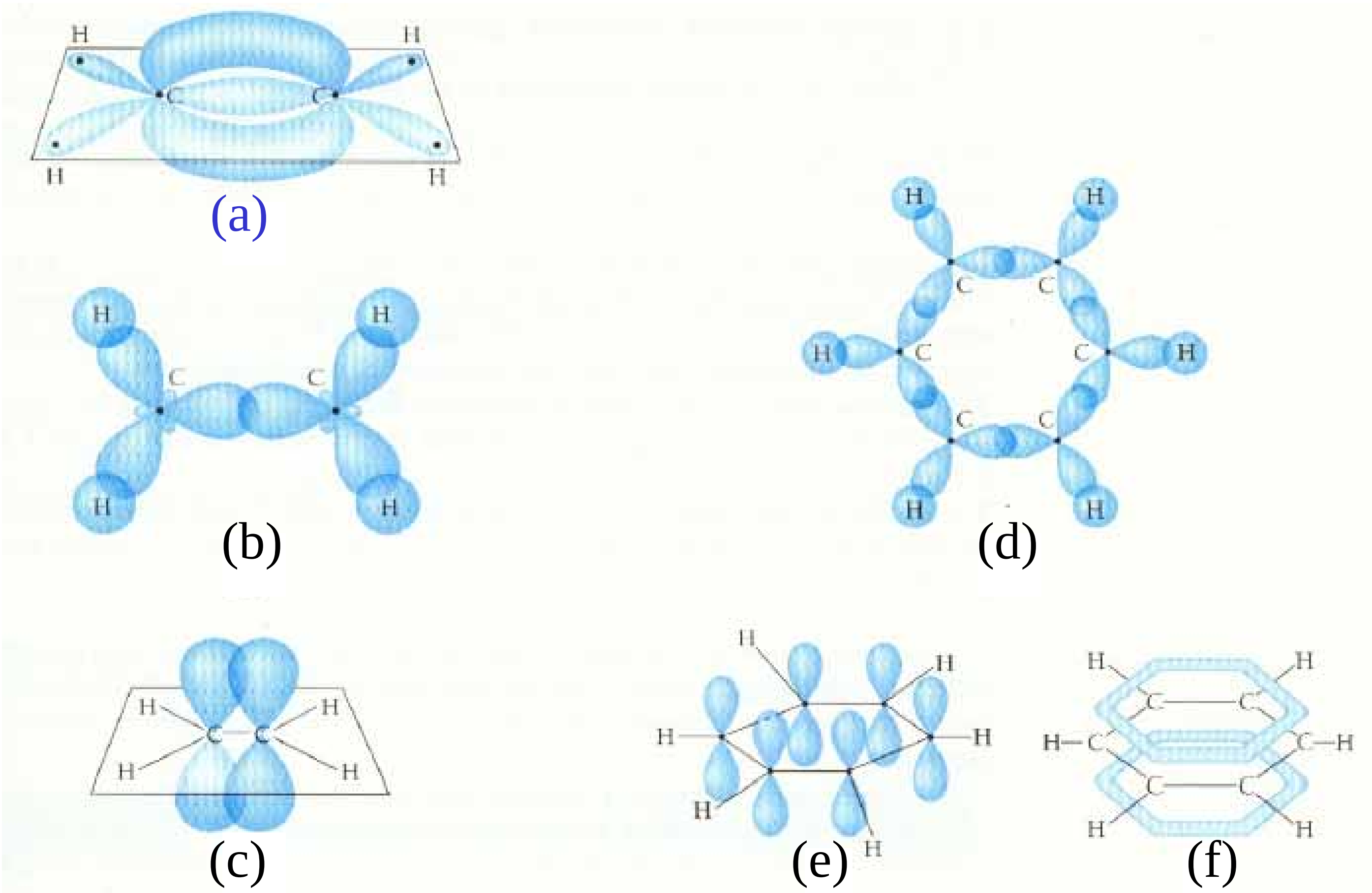
What is a carbon ?

- Sixth element in periodic table: occupy $1s^2$, $2s^2$, $2p^2$ atomic orbitals
- $1s^2$ contains two strongly bound core electrons; $2s^2$, $2p^2$ contains four weakly bound valence electrons
- Due to small energy difference btw $2s$ and $2p$ → hybridization of $2s$ and $2p$ orbitals: sp^n with n = 1,2,3
- Formation of σ and π bonding molecular orbitals from s and p atomic orbitals :



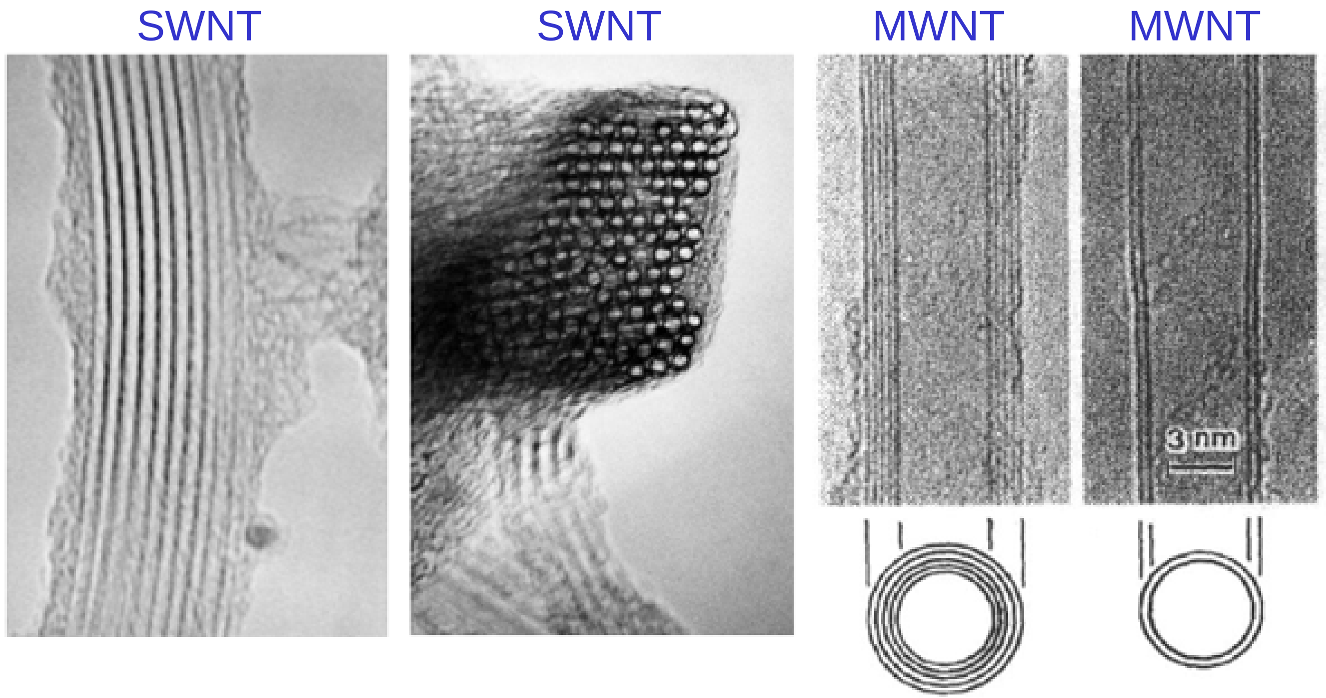
Molecular orbital

- Ethylene (C_2H_4) molecule. (a) All the atoms lie in a plane perpendicular to the plane of the paper. (b) Top view, showing the sp^2 hybrid orbitals that form σ bonds. (c) Side view, showing the pure p_z orbitals that form a π bond between the C atoms.
- Benzene (C_6H_6) molecule. (a) s bonds between C atoms and C-H atoms. (b) Each C atom has a pure p_z orbitals occupied by one electron. (c) The bonding π molecular orbitals formed by the six p_z atomic orbitals constitute a continuous electron probability distribution around the molecule that ontains six delocalized electrons.



What is a carbon nanotube?

- Discovered by Sumio Iijima (NEC) in his study of arc-discharge products.
- Nanotube is a fullerene molecule elongated in the axial direction, forming a tubule structure.
- Single-wall carbon nanotube (SWNT): rolled-up single sheet of graphene (d_t < 3 nm)
- Multi-wall carbon nanotube (MWNT): coaxially rolled-up multiply sheets of graphene (d_t > 3 nm)



Why is it special ?

Geometrical structure

↓

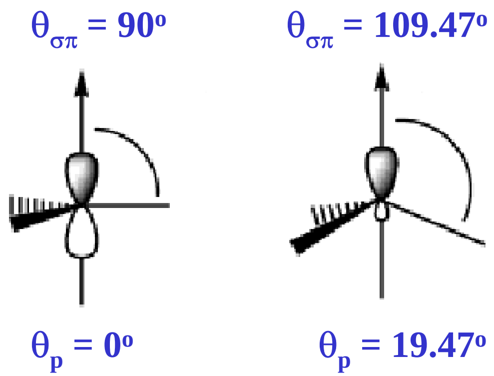
Chirality (or say Helicity)

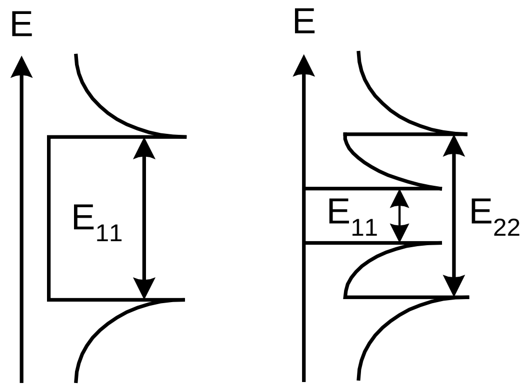
↓

Electronic structure

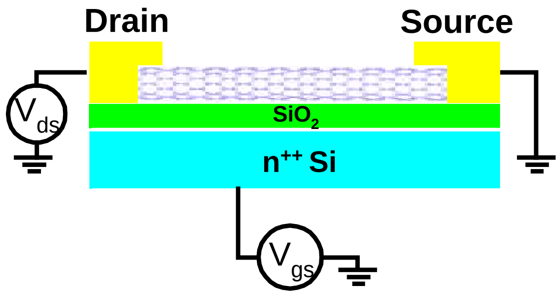
↙ ↓ ↘

Chemical properties | Optical properties | Transport properties



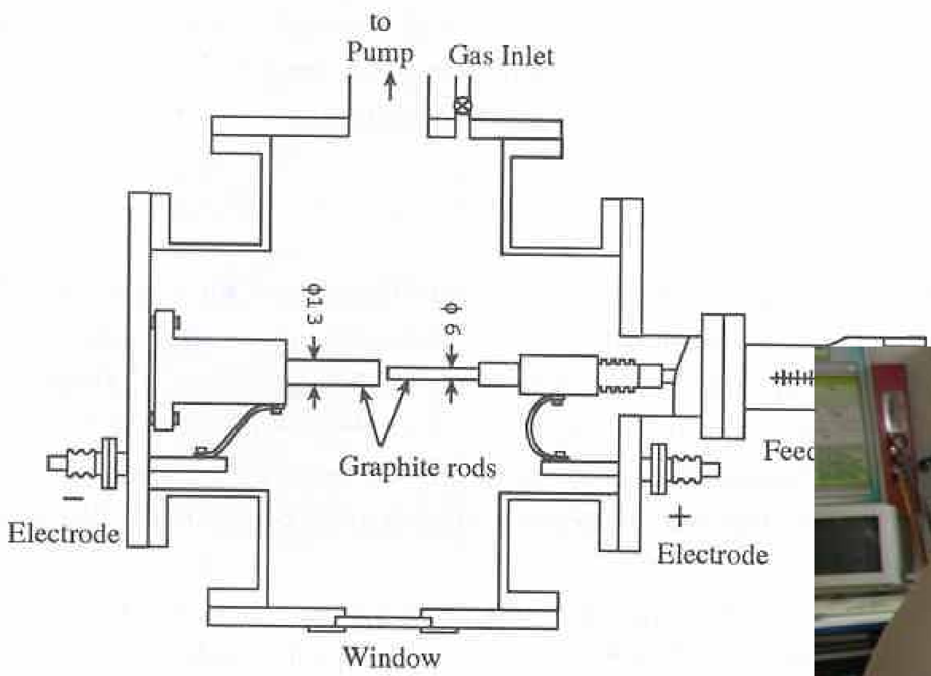


metal **semiconductor**



Synthesis – arc discharge

Kräschmer generator

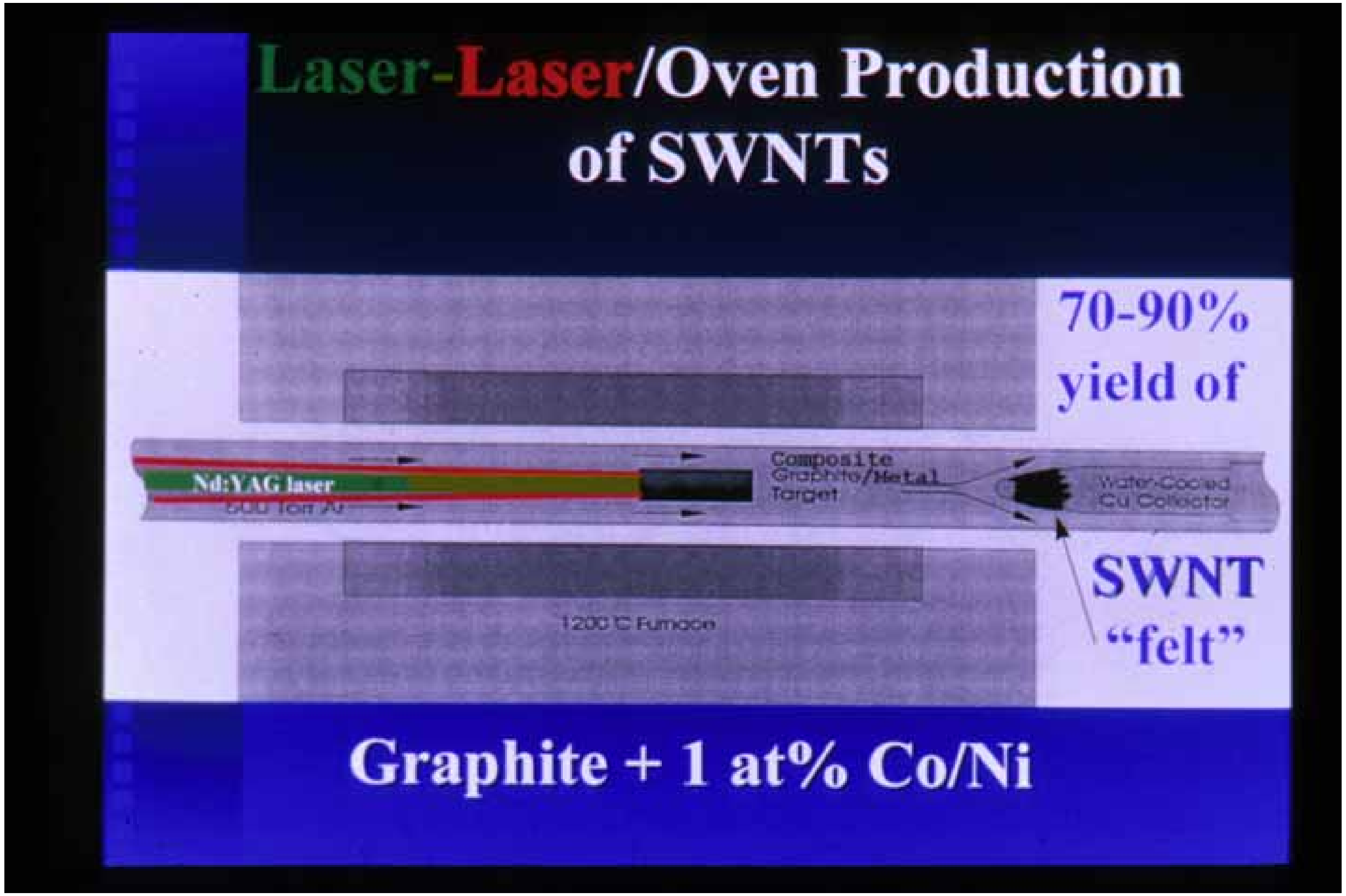


1. Close to the melting T of graphite (3000~4000 degree)

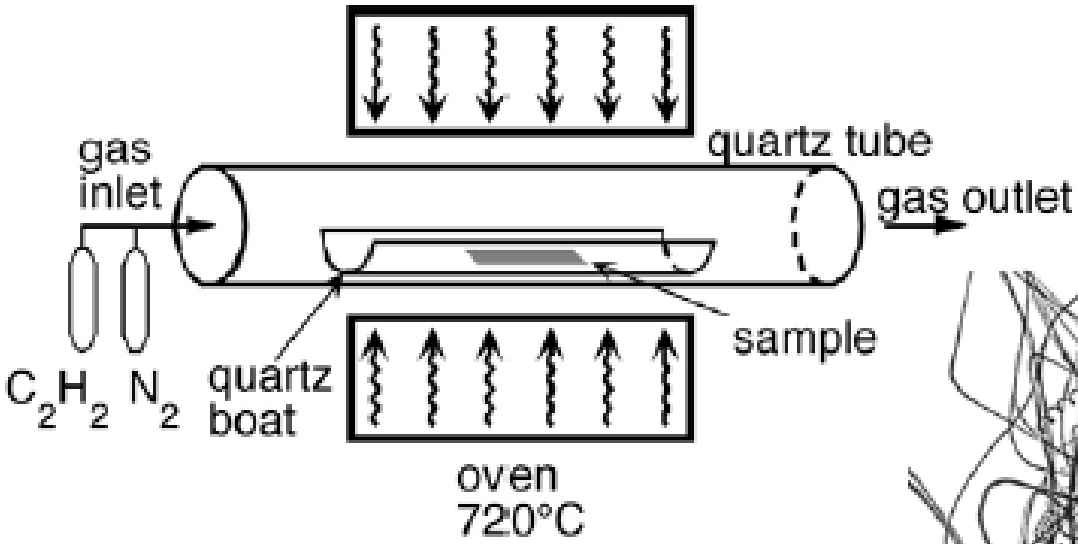
2. Carbon are evaporated by He^{+} plasma

Catalyst:
- transition metals (Fe, Co, Ni)
- non-magnetic (RhPd)

Synthesis – laser ablation

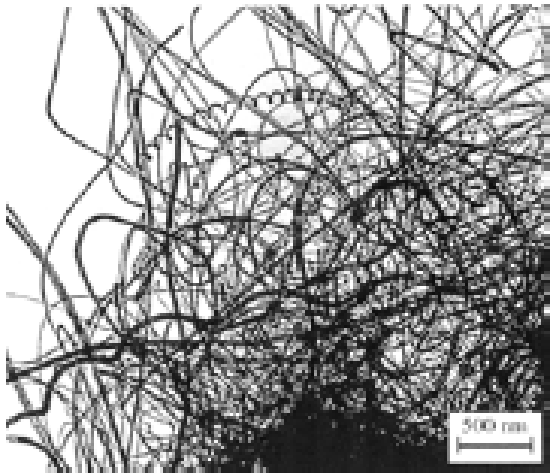


Synthesis – chemical vapor deposition

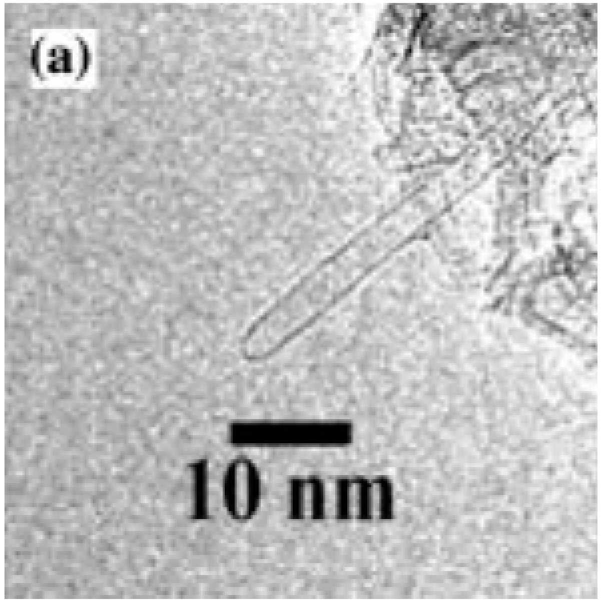


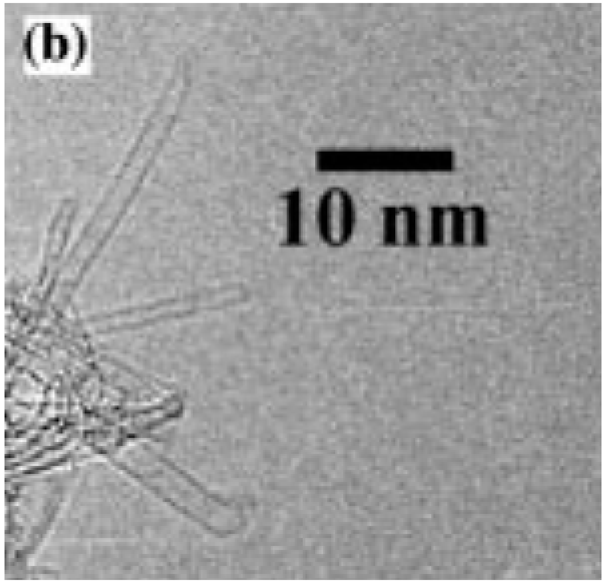
(or higher, i.e. 900 °C)

Hernadi et al., Catalysis Lett. 59, 229 (1997)

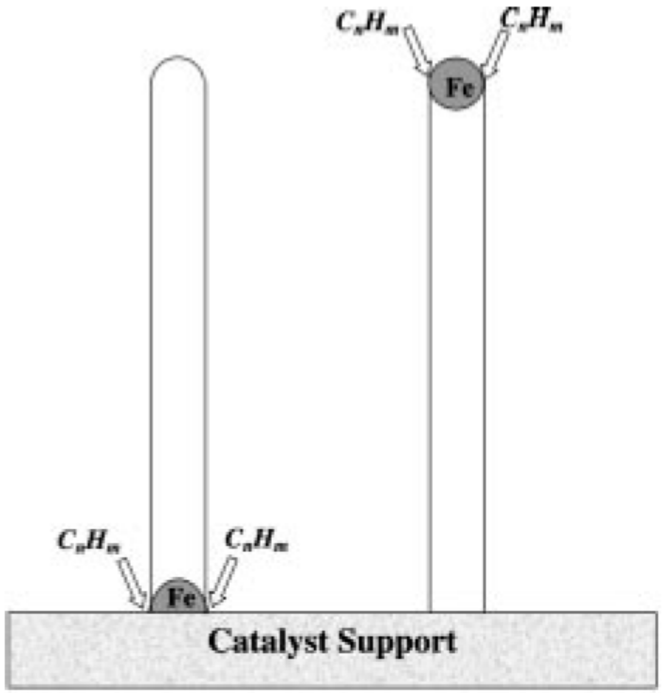


Growth mechanism of CVD method



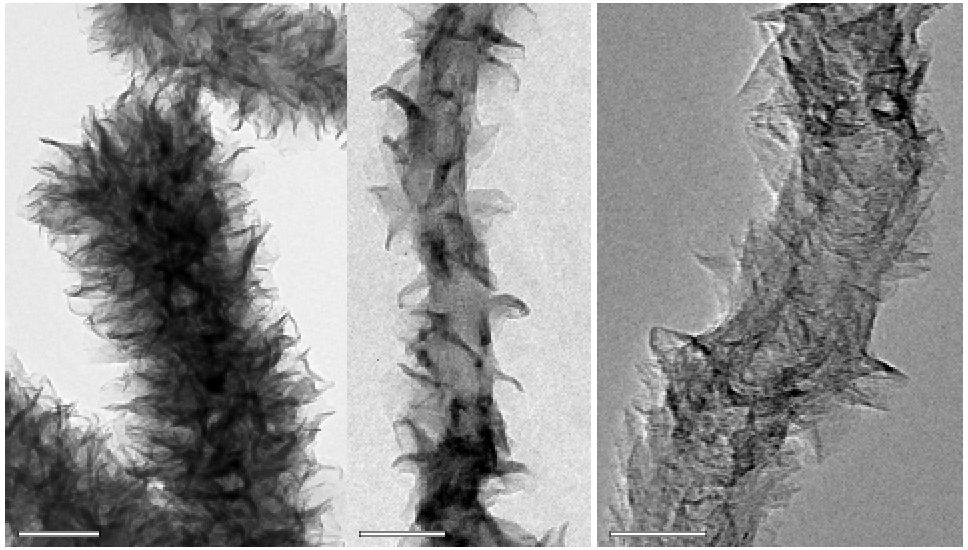


1. Dissociation of hydrocarbon by catalysts
2. Dissolution and saturation of carbon in catalysts
3. Precipitation on the catalysts
4. Important growth parameters: Type of hydrocarbon, catalyst, temperature

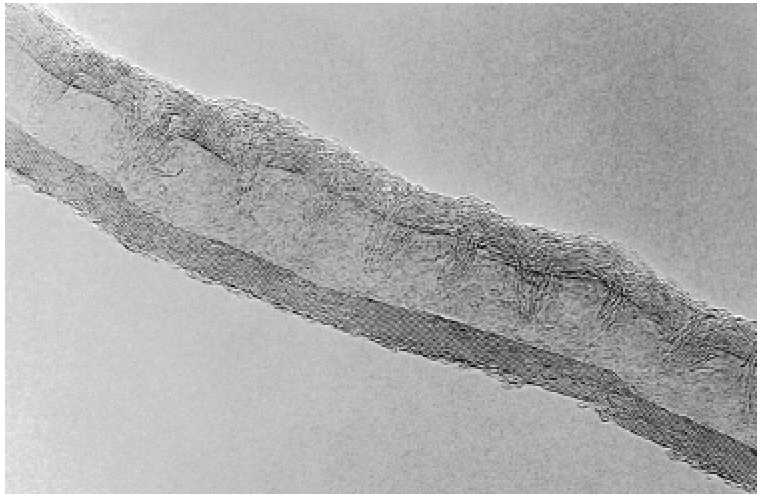


CVD growth

Barbed wires



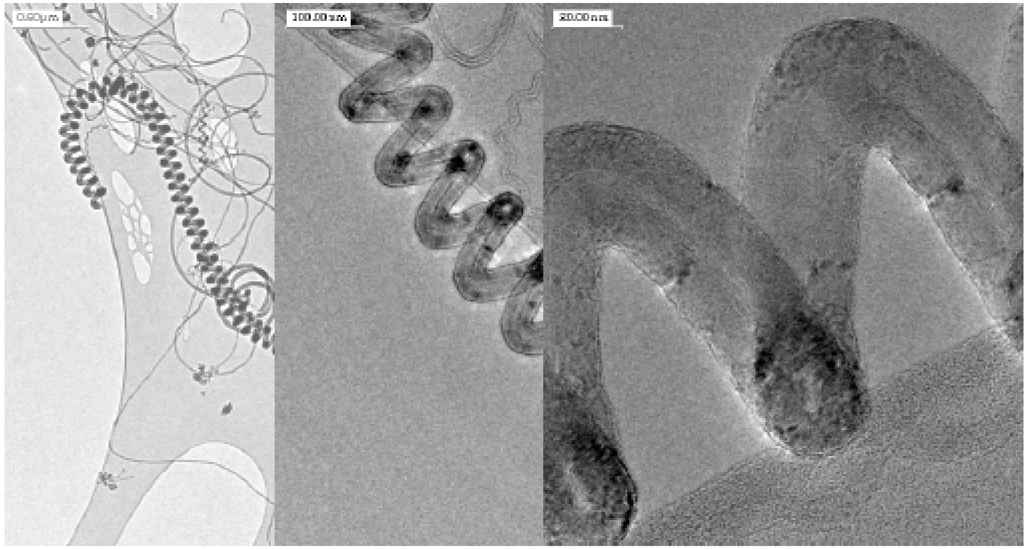
Hairy nanotube



CVD growth

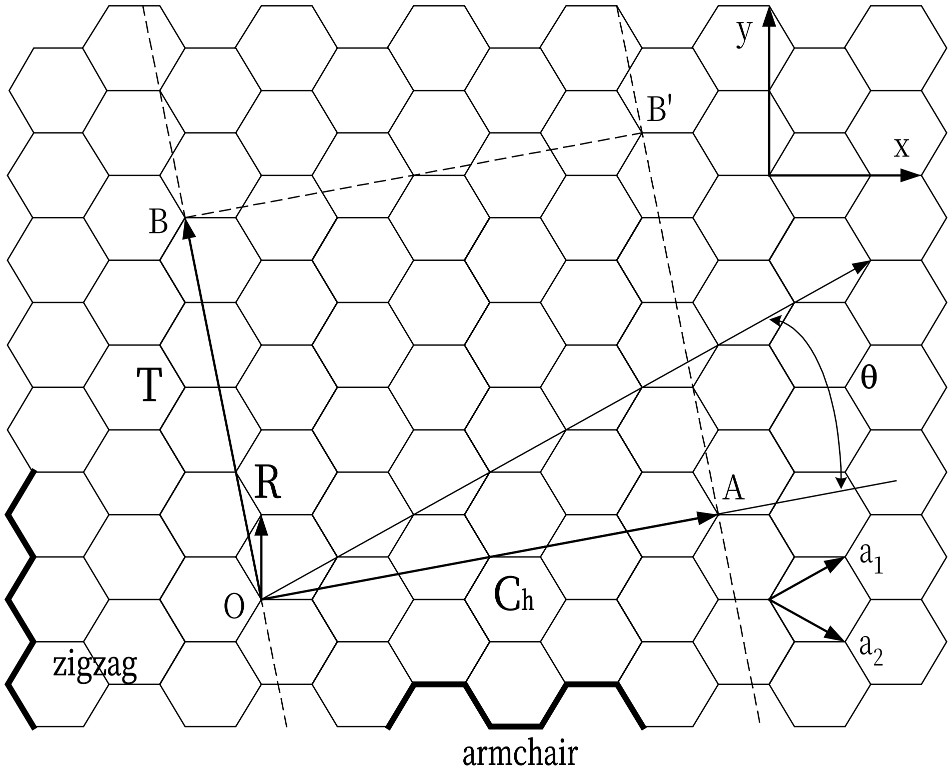
Bamboo nanotubes

Nanotube Spirales

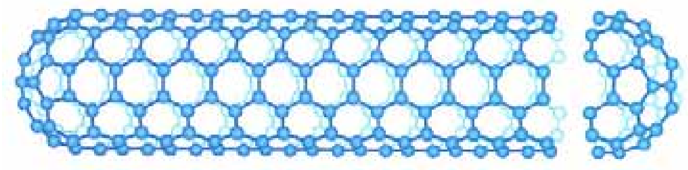


Geometrical structure of nanotubes

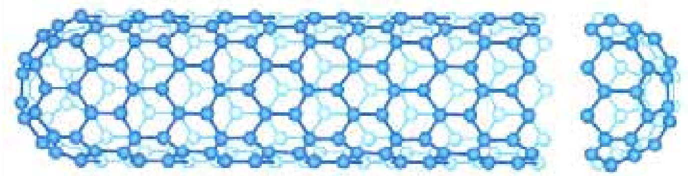
Graphene hexagonal network



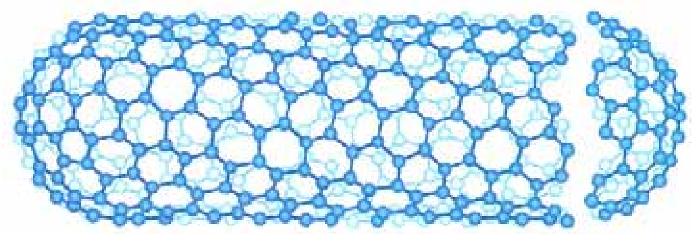
(n,m)=(5,5)



(n,m)=(9,0)



(n,m)=(10,5)

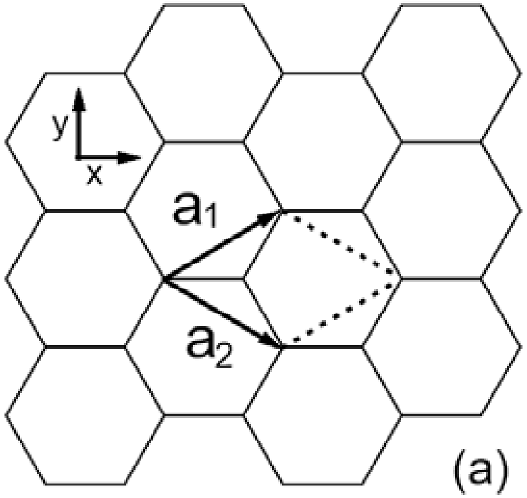


Chiral Angle : **θ**

- zigzag **θ** =0
- armchair **θ** = **π**/6
- chiral 0< **θ** < **π**/6

Electronic structure

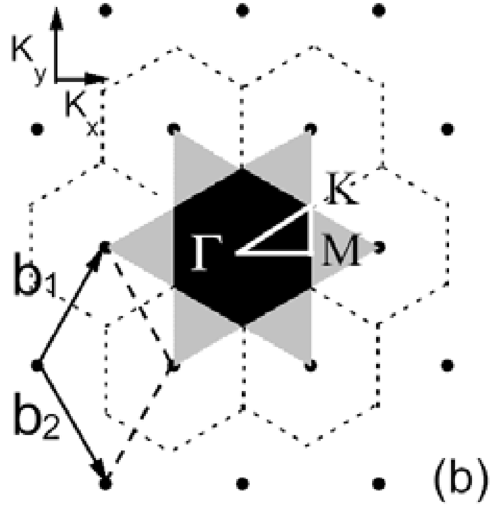
Real lattice



$$\mathbf{a_1} = (\sqrt{3}a/2, a/2)$$

$$\mathbf{a_2} = (\sqrt{3}a/2, -a/2)$$

Reciprocal lattice



$$\mathbf{b_1} = (2\pi/\sqrt{3}a, 2\pi/a)$$

$$\mathbf{b_2} = (2\pi/\sqrt{3}a, -2\pi/a)$$

$$\mathbf{C_h} = n\mathbf{a_1} + m\mathbf{a_2} \equiv (n, m)$$

$$\mathbf{T} = t_1\mathbf{a_1} + t_2\mathbf{a_2} \equiv (t_1, t_2)$$

$C_h K_1 = 2\pi$
$C_h K_2 = 0$
$T K_1 = 0$
$T K_2 = 2\pi$

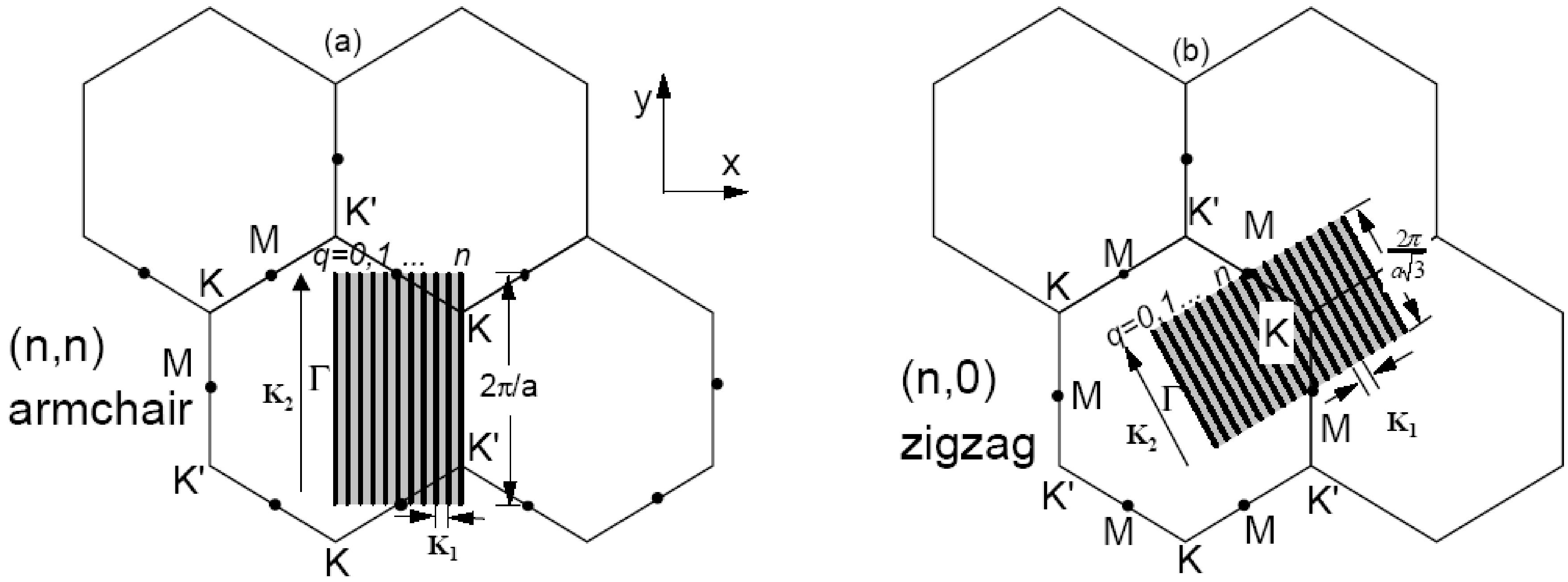
$$\mathbf{K_1} = (-t_2\mathbf{b_1} + t_1\mathbf{b_2})/N$$

$$\mathbf{K_2} = (m\ \mathbf{b_1} - n\mathbf{b_2})/N$$

Electronic structure

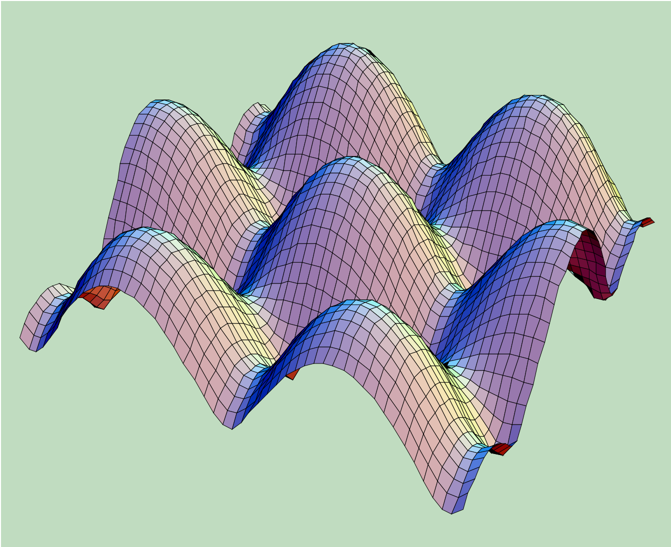
- Nanotube axis direction : 1D wave vectors *k* (continuous)
- Nanotube circumferencial direction : momentum quantization (N cutting lines)

$$\mathbf{K} = k\frac{\mathbf{K_2}}{|\mathbf{K_2}|} + \mu\mathbf{K_1} \qquad \mu = 0, \ldots N-1 \ \text{ and } \ -\pi/|\mathbf{T}| < k < \pi/|\mathbf{T}|$$



Electronic structure

π* band



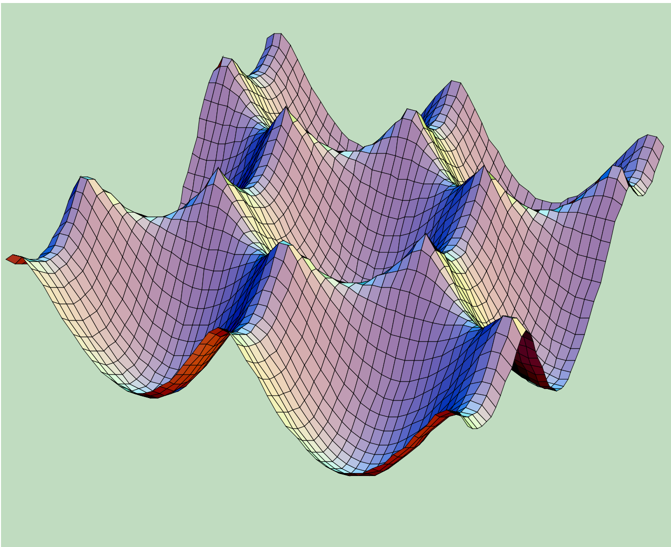
Energy dispersion of graphene

$$E^{\pm}_{g2D}(k) = \frac{\epsilon_{2p} \pm \gamma_0 \omega(k)}{1 \mp s\omega(k)}$$

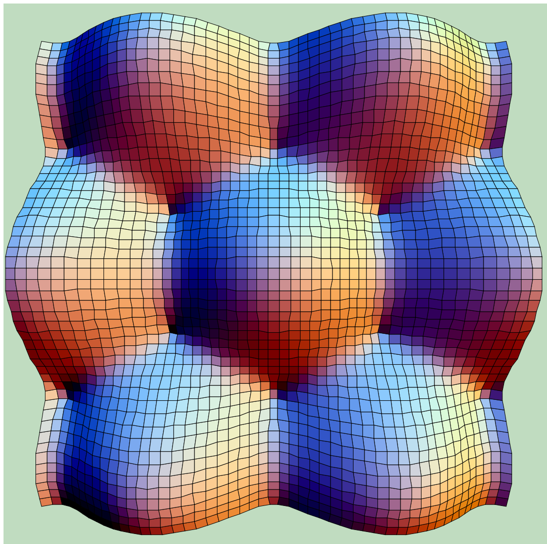
$$\omega(k) = \{1 + 4\cos(\frac{\sqrt{3}k_x a}{2})\cos(\frac{k_y a}{2}) + 4\cos^2(\frac{k_y a}{2})\}^{1/2}$$

γ_0 : the energy overlap integral
ε_{2p} : the site energy of 2p atomic orbital
s : the overlap of electronic wave function
a = 3 $^{1/2}$ a_0 ,a_0 = the nearest neighbor distance (0.142 nm)

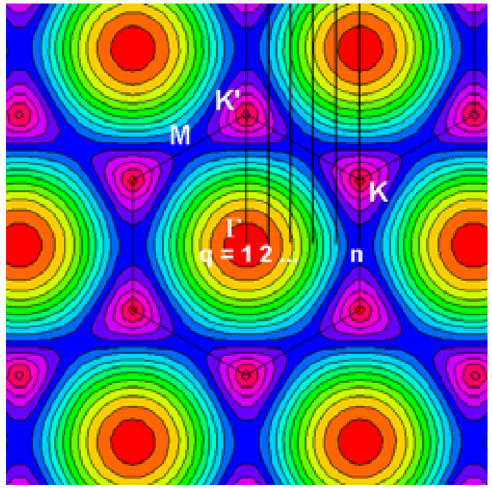
π band



Top view



Projection (energy counter)



Electronic structure

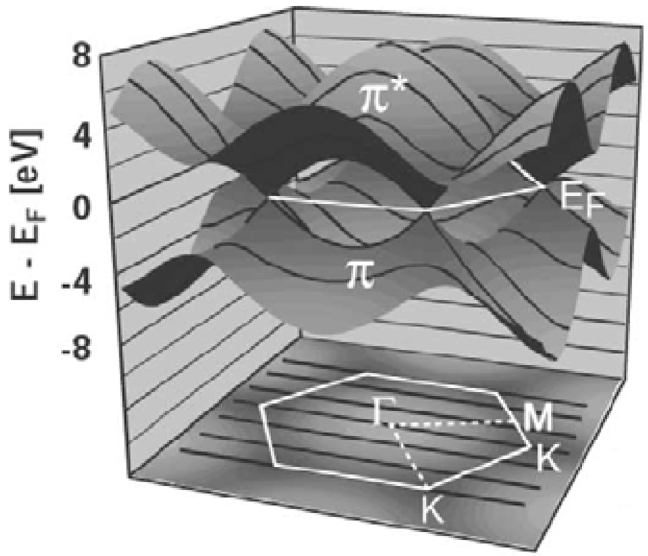
Energy dispersion of 1D nanotube

$$E^{\pm}_{1D}(\mathbf{K}) = E^{\pm}_{g2D}(k\frac{\mathbf{K_2}}{|\mathbf{K_2}|} + \mu\mathbf{K_1})$$

$\mu = 0, ...N-1$ and $-\pi/|\mathbf{T}| < k < \pi/|\mathbf{T}|$

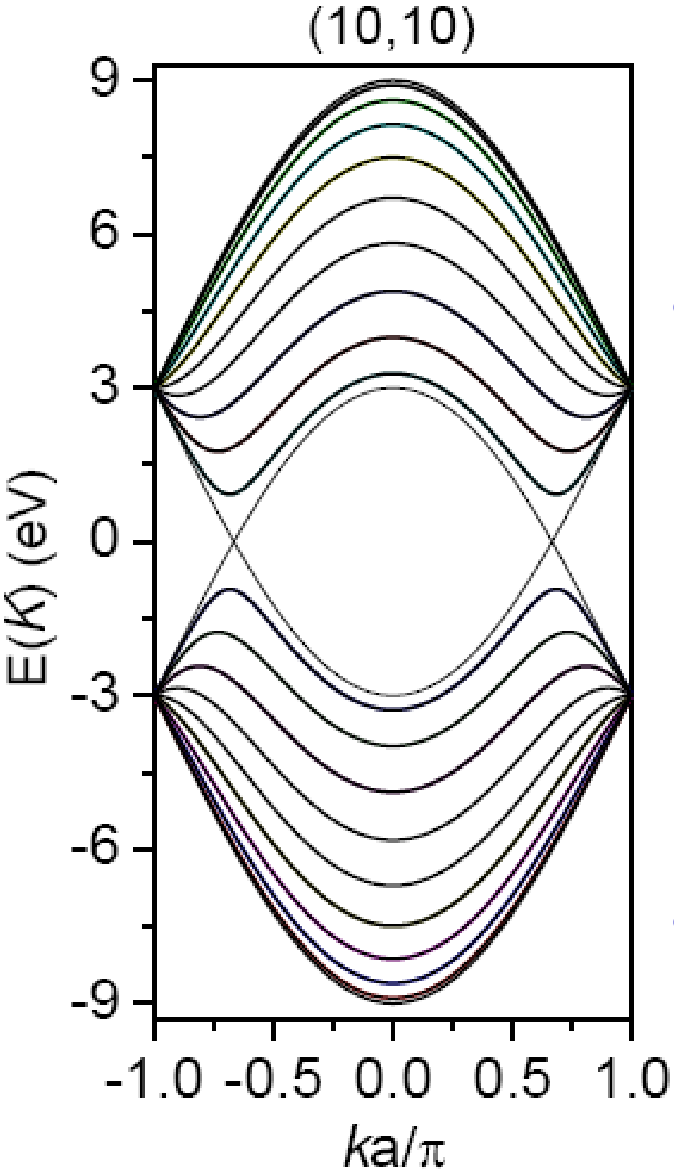
(μ is discrete) (k is continuous)

2D dispersion



→

1D dispersion



20 π* bands

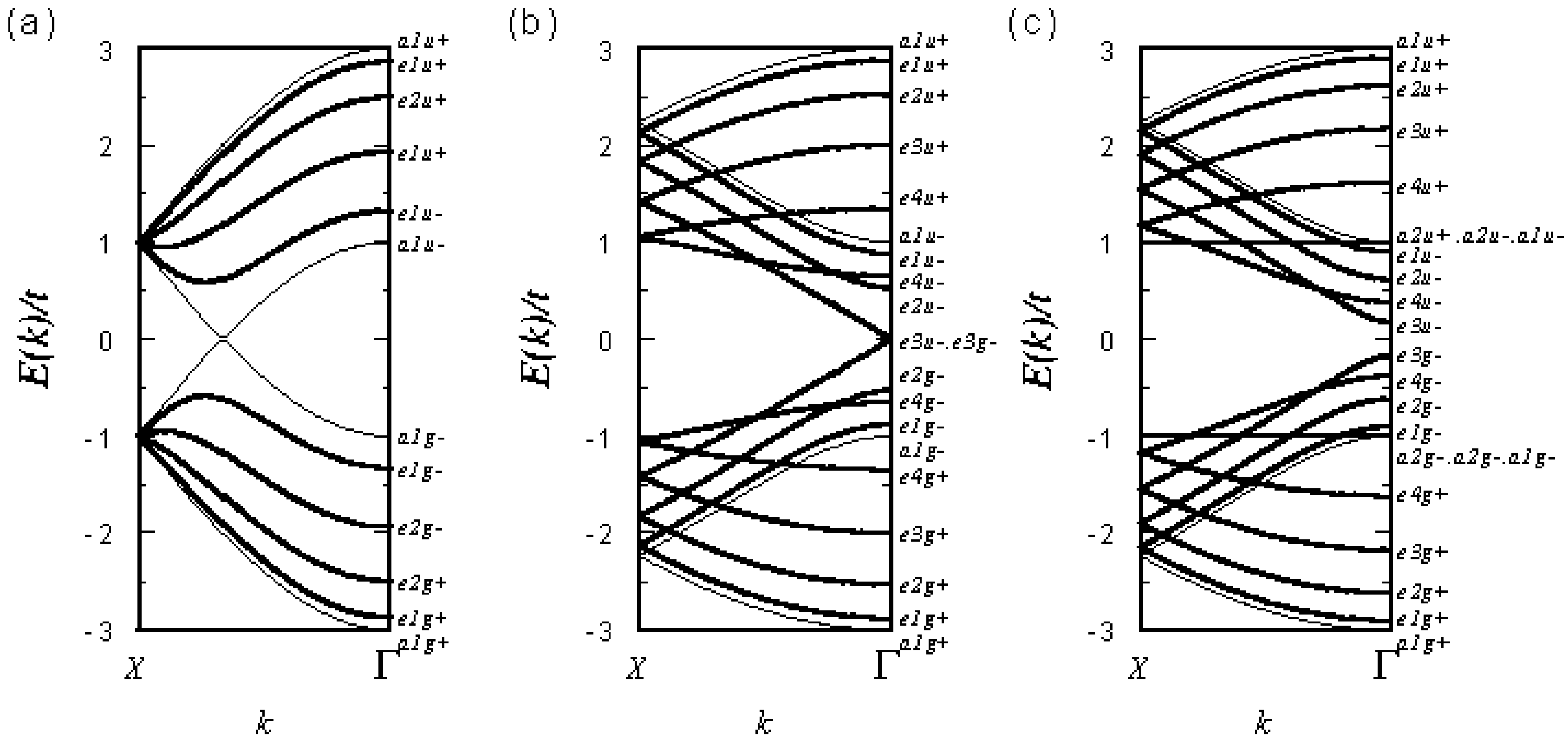
(9 bands doubly degenerate)

20 π bands

(9 bands doubly degenerate)

1D DOS

(5 , 5) (9 , 0) (10 , 0)



N = 10 for (5,5) nanotube: 10 bonding/antibonding bands, four of which are doubly degenerate (thick solid lines)

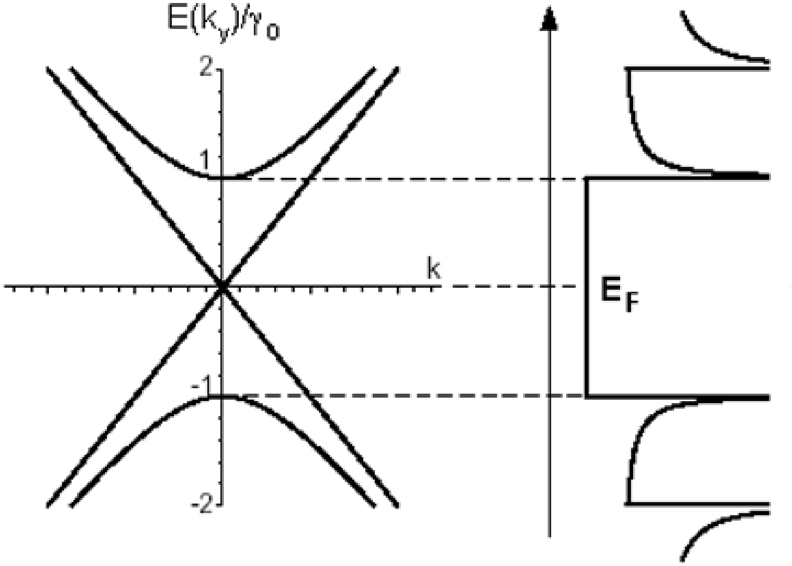
N = 18 for (9,0) nanotube: 18 bonding/antibonding bands, eight of which are doubly degenerate (thick solid lines)

N = 20 for (10,0) nanotube: 20 bonding/antibonding bands, nine of which are doubly degenerate (thick solid lines)

R. Saito *et al.*, *Phys. Rev*. B **46**, 1804 (1992)

1D DOS

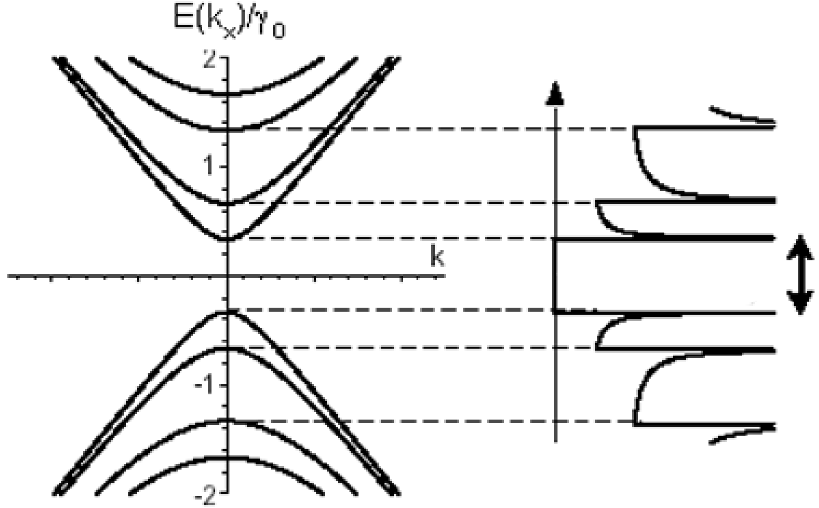
Metallic nanotube



$E_g \sim 6\gamma_0 a_{c\text{-}c}/d_t$

(With finite DOS in E_g)

Semiconducting nanotube



$E_g \sim 2\gamma_0 a_{c\text{-}c}/d_t$

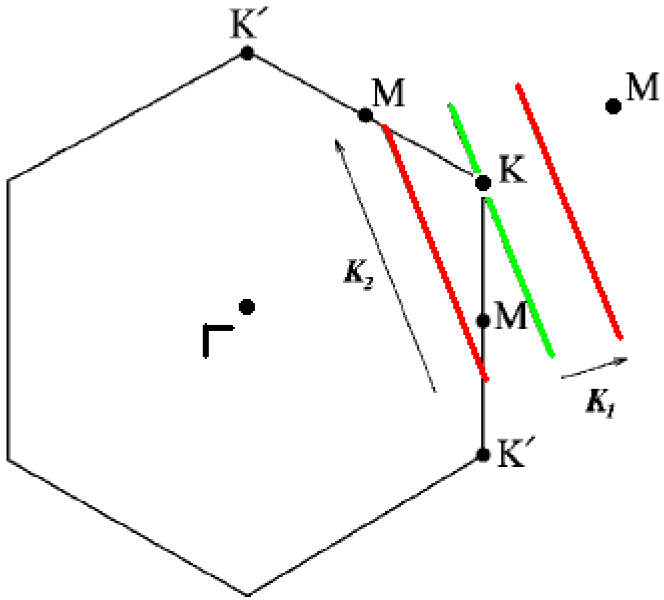
(Without DOS in E_g)

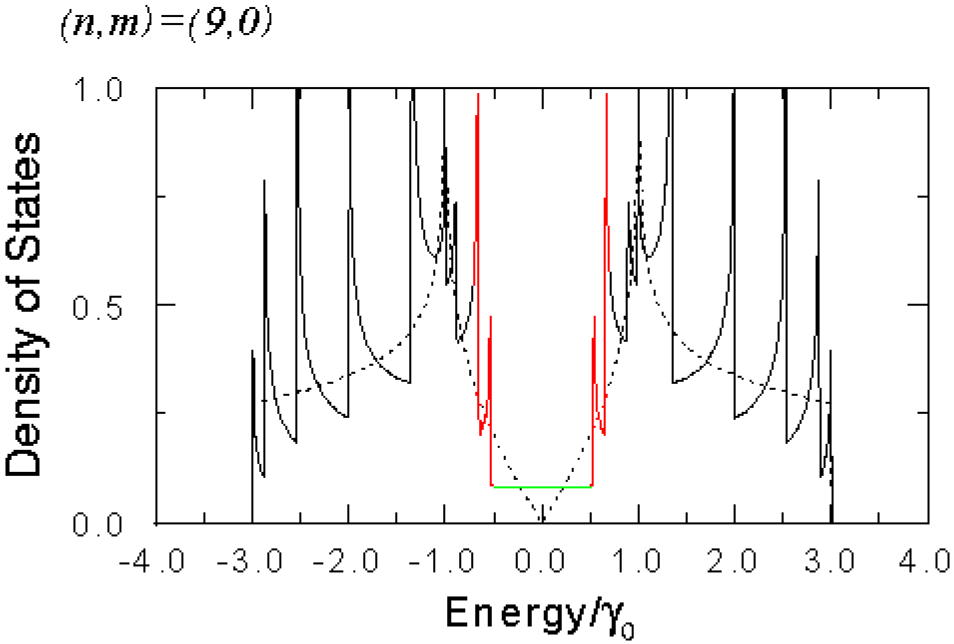
$$n - m = \begin{cases} 3p & \text{metal} \\ 3p \pm 1 & \text{semiconductor} \end{cases}$$

1D DOS

Metallic nanotube :

1D energy dispersion :
- K point always lies on cutting lines
- inequivalent in two neighboring lines (DOS splitting)



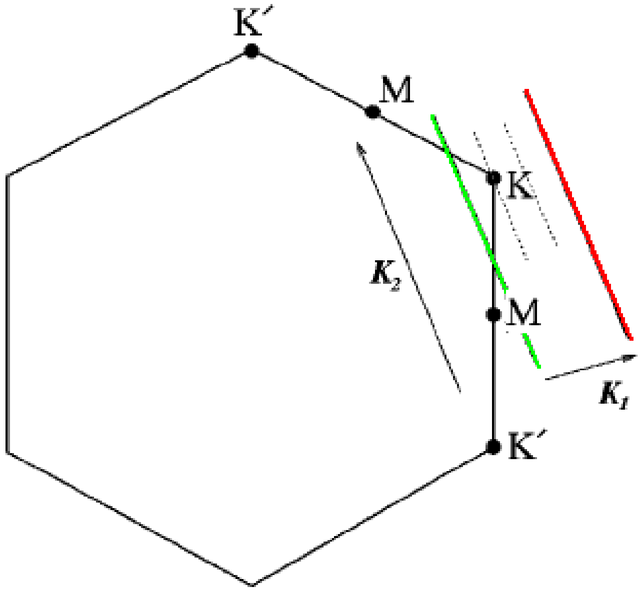


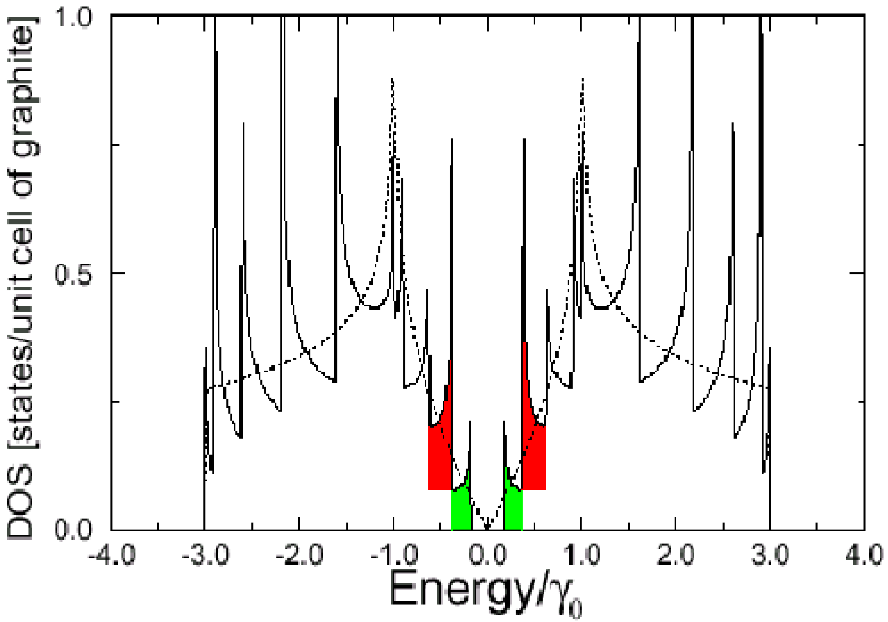
R. Saito *et al*, *Phys. Rev. B* **61**, 2981(2000)

1D DOS

Semiconducting nanotube :

1D energy dispersion :
- K point always lies 1/3 or 2/3 away from cutting lines
- no DOS splitting





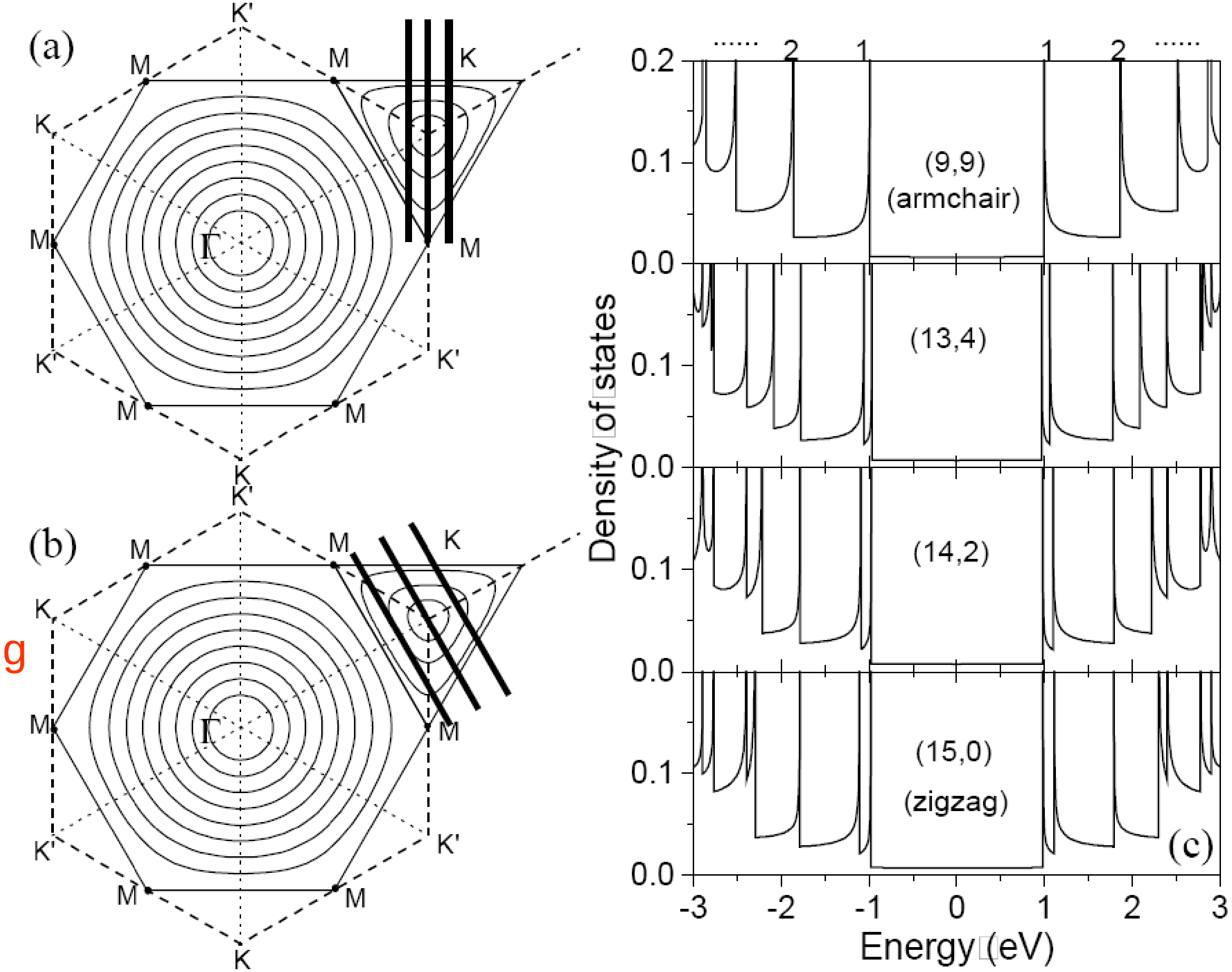
R. Saito *et al*, *Phys. Rev. B* **61**, 2981(2000)

1D DOS

Magnitude of DOS splitting depends on chirality

Armchair:
No DOS splitting

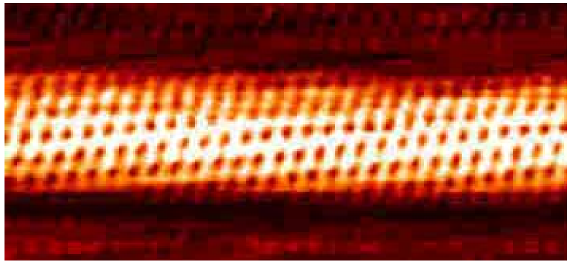
Zigzag:
Max DOS splitting

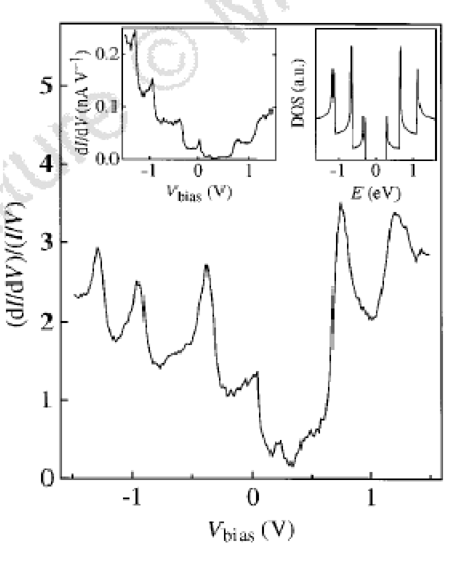


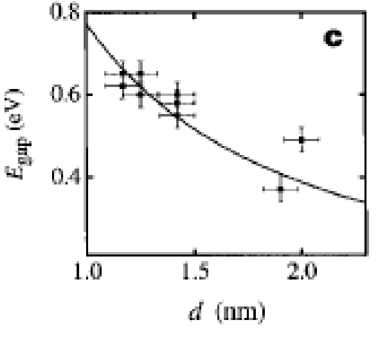
1D DOS

Experiment 1:

STM on single-wall carbon nanotube
Prove the 1D DOS



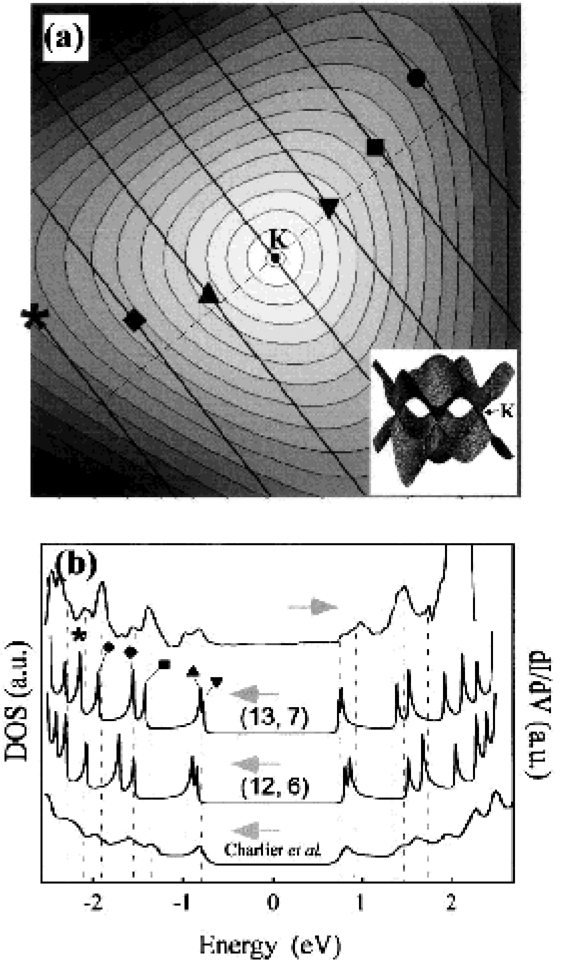




J. W. G. Wildoer *et al*, Nature 391, 59 (1998).

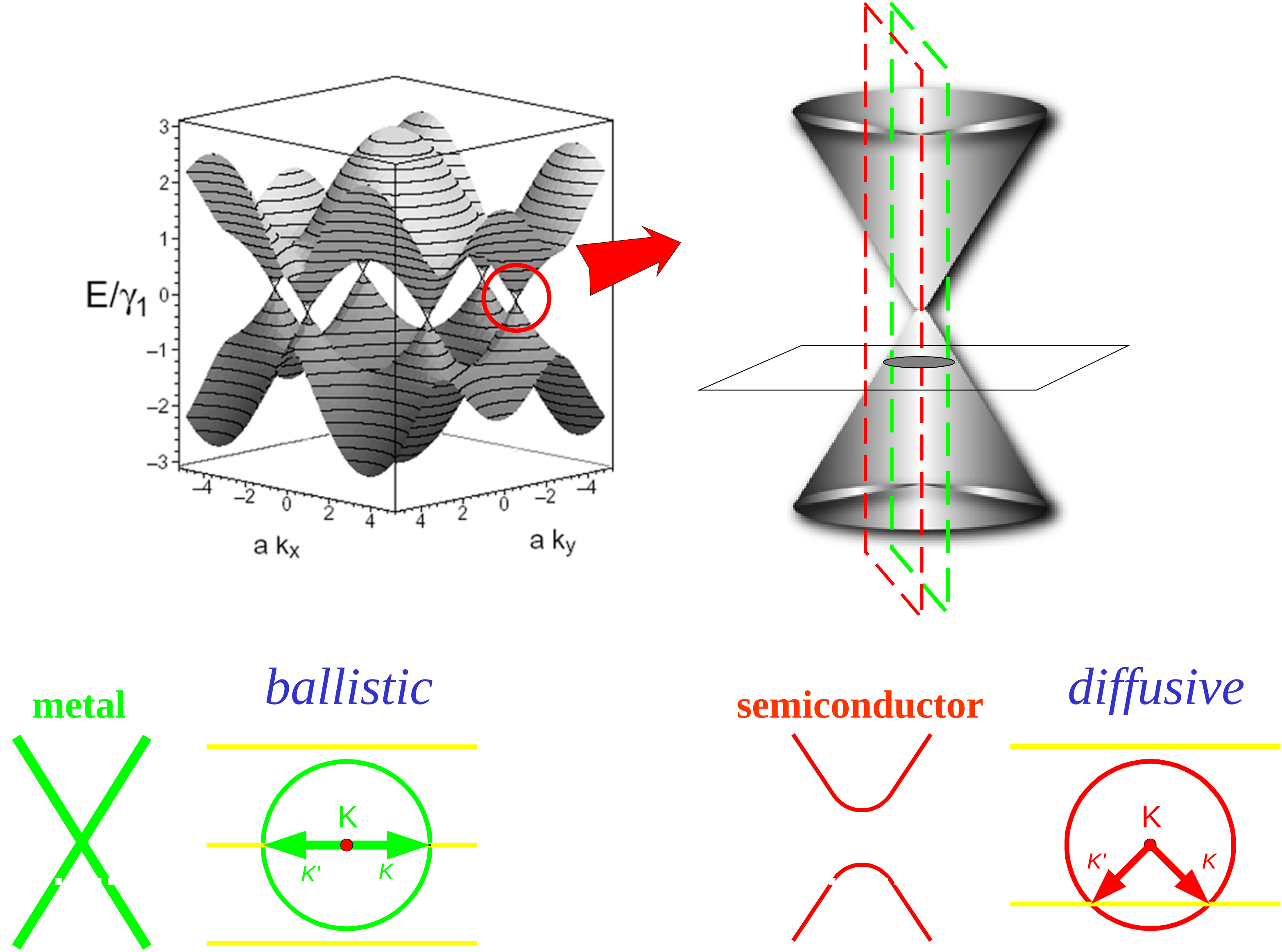
Experiment 2:

STM on single-wall carbon nanotube
Prove the splitting of 1D DOS



P. Kim *et al.*, PRL 82, 1225 (1999).

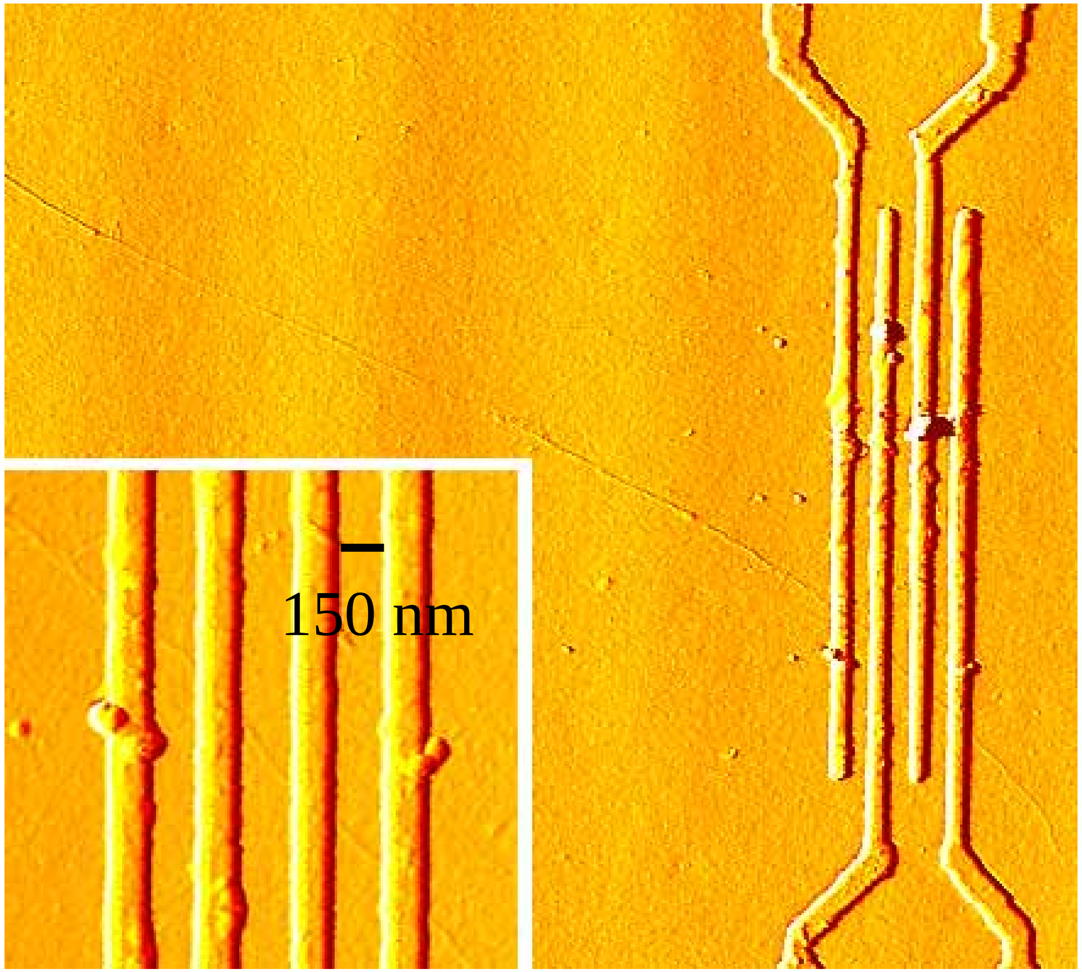
Fermi circle



Contact a nanotube – tube on top

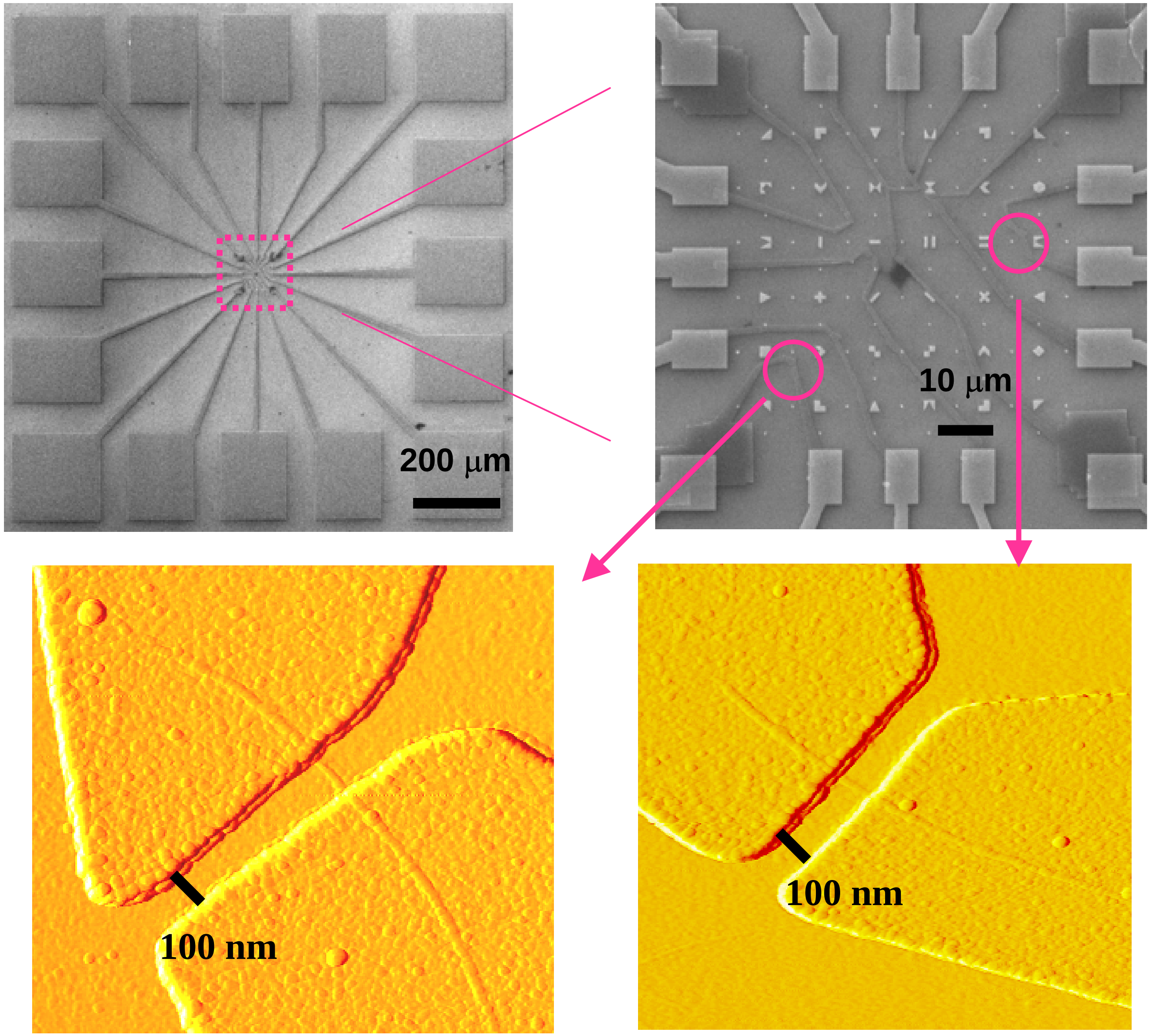
CNT absorption on Si substrate
with predefined electrode arrays

Device fabrication depends on God ...

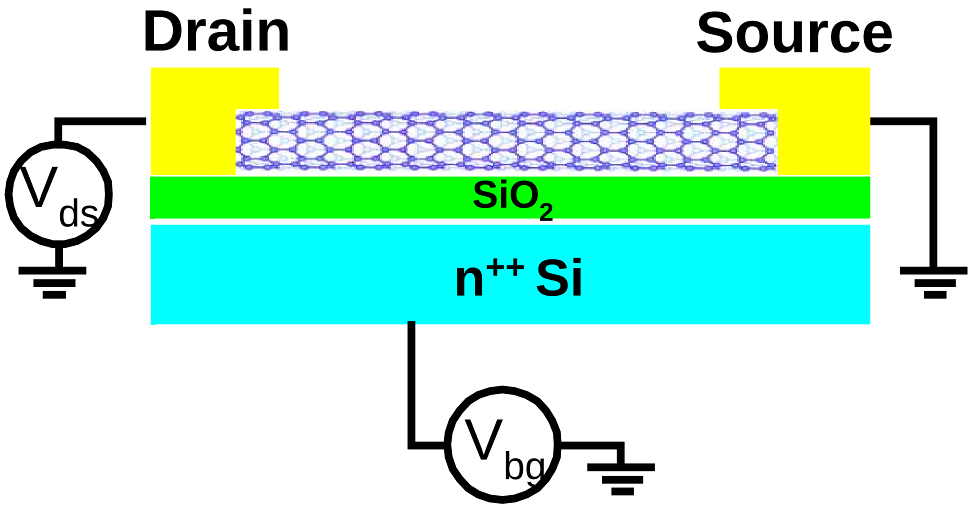


Contact a nanotube – metal on top

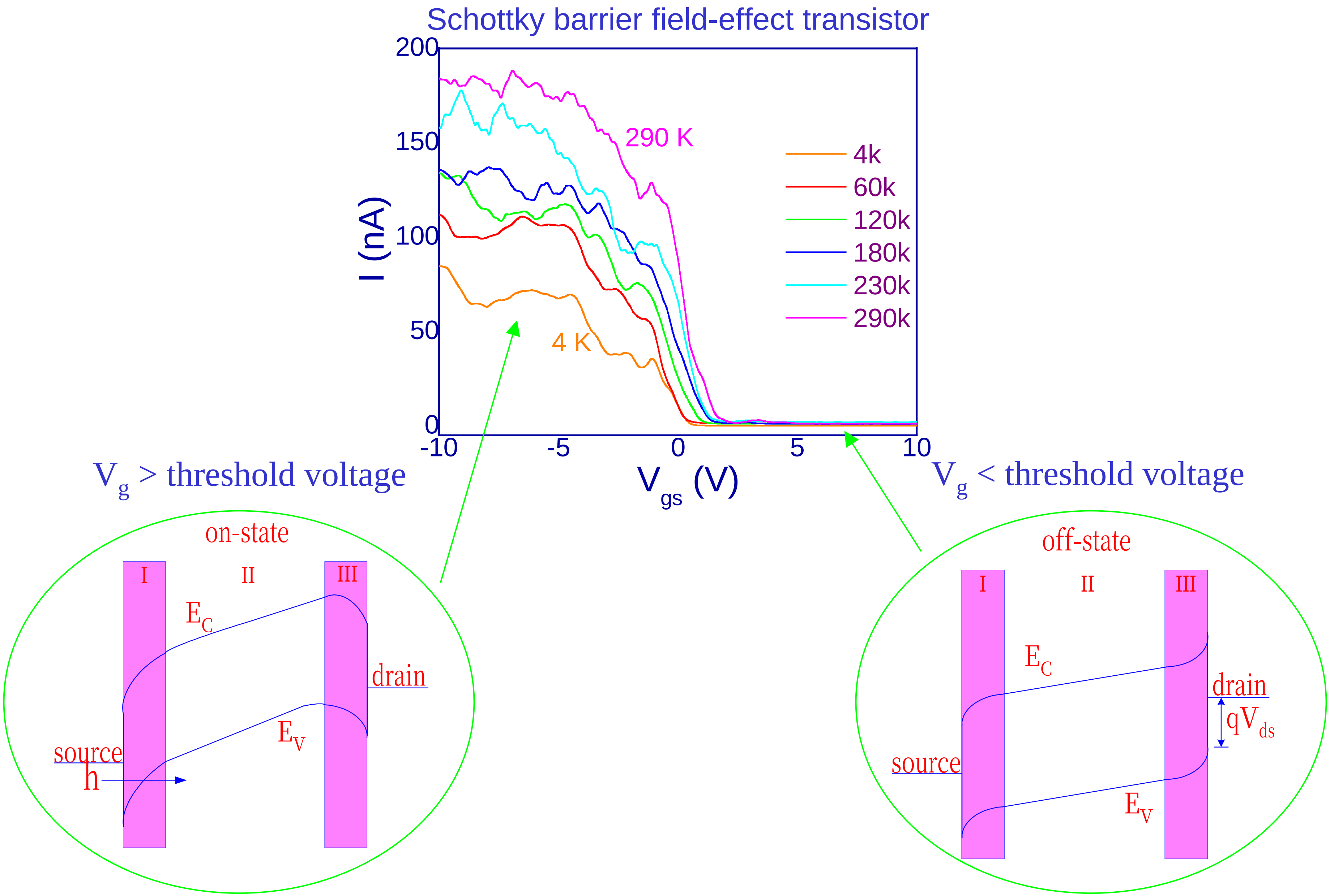
A professional way :



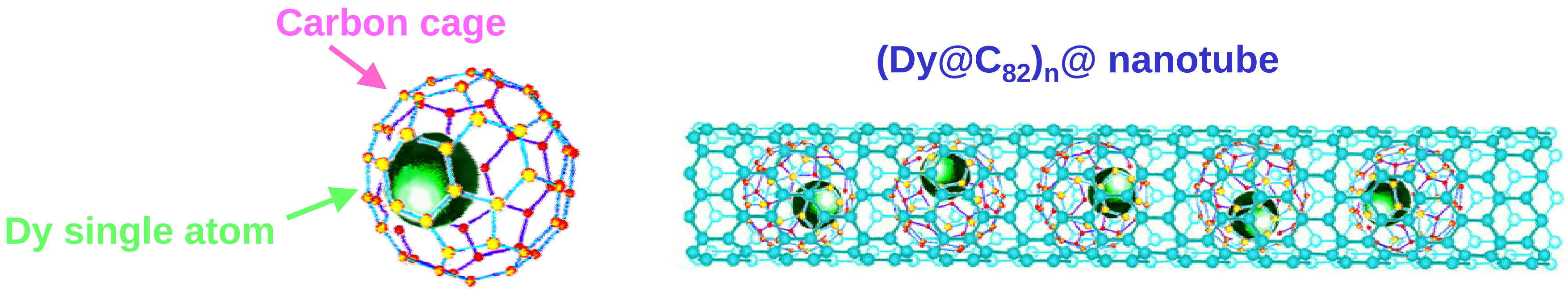
Transport on an individual nanotube

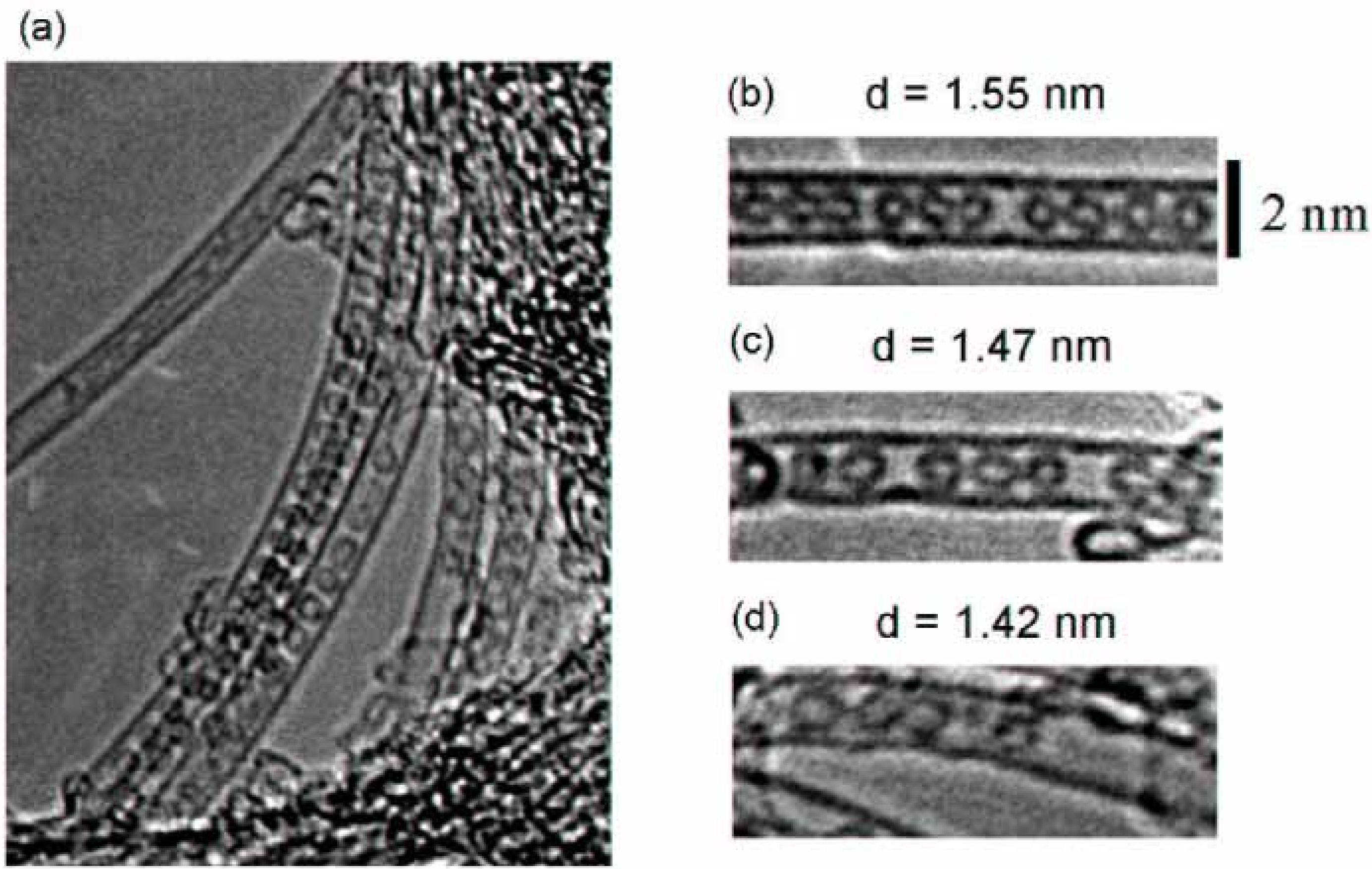


Conduction in semiconducting nanotubes



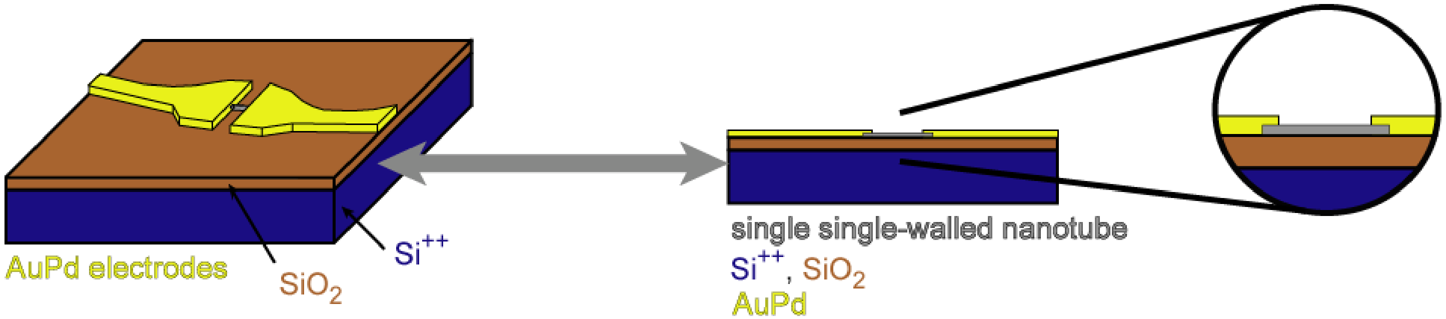
Bandgap madulation (I) - peapods



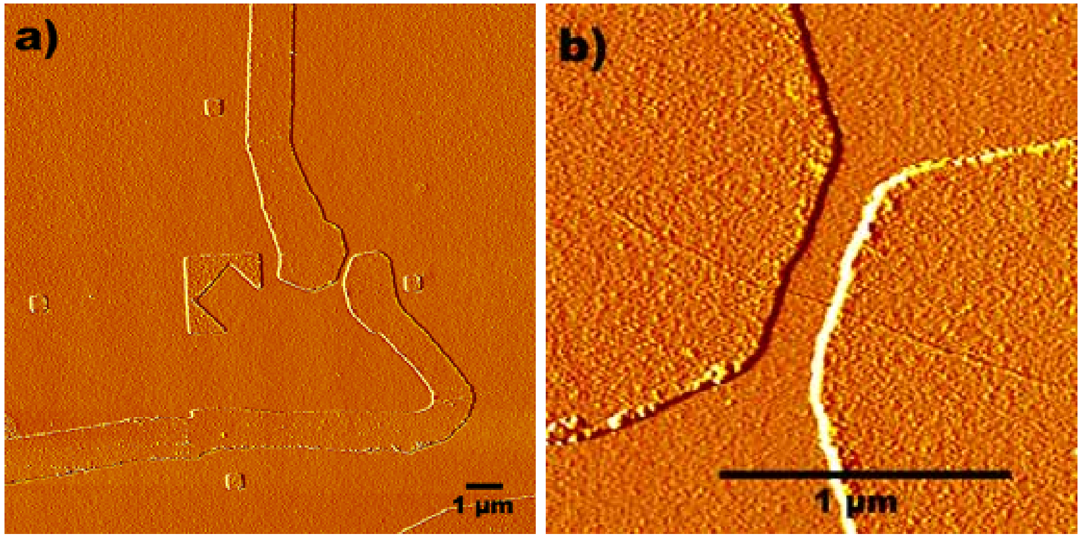


Bandgap madulation (I) - peapods

- Peapod production by filling SWNTs from gas phase.
- SWNTs or peapods are dispersed and adsorbed onto Si/SiO_2 substrates.
- Sample after standard e-beam process (approx. 30nm AuPd):

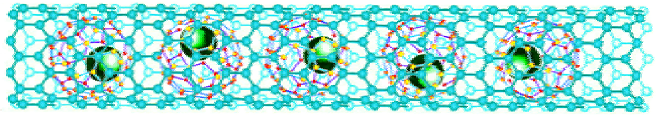


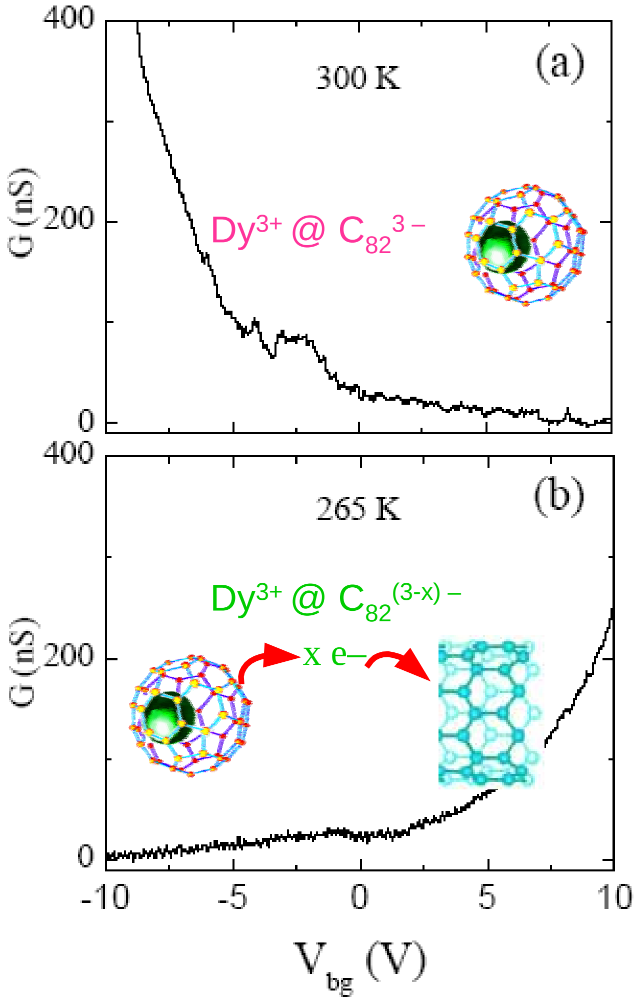
- „single“ SWNT after putting contacts (utilizing a marker system)



Bandgap madulation (I) - peapods

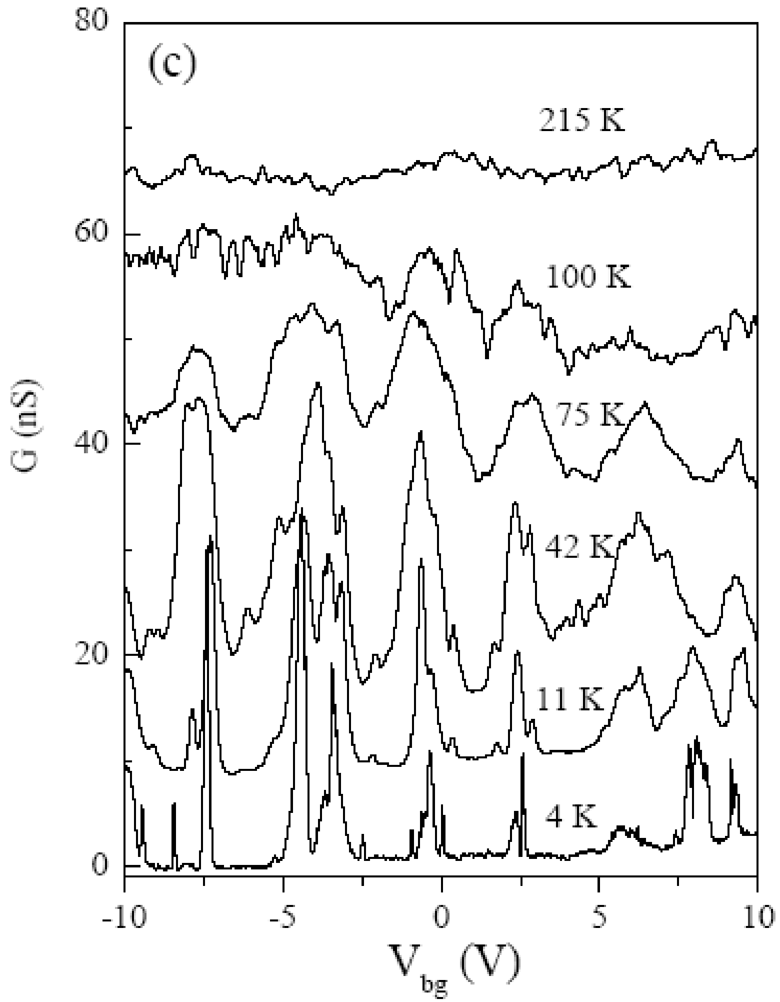
Semiconducting peapod





Temperature-dependent conduction mechanisms

p-type → n-type → metal



P. W. Chiu *et al*, Appl. Phys. Lett. 79, 3845 (2001).

Bandgap madulation (I) - peapods

?

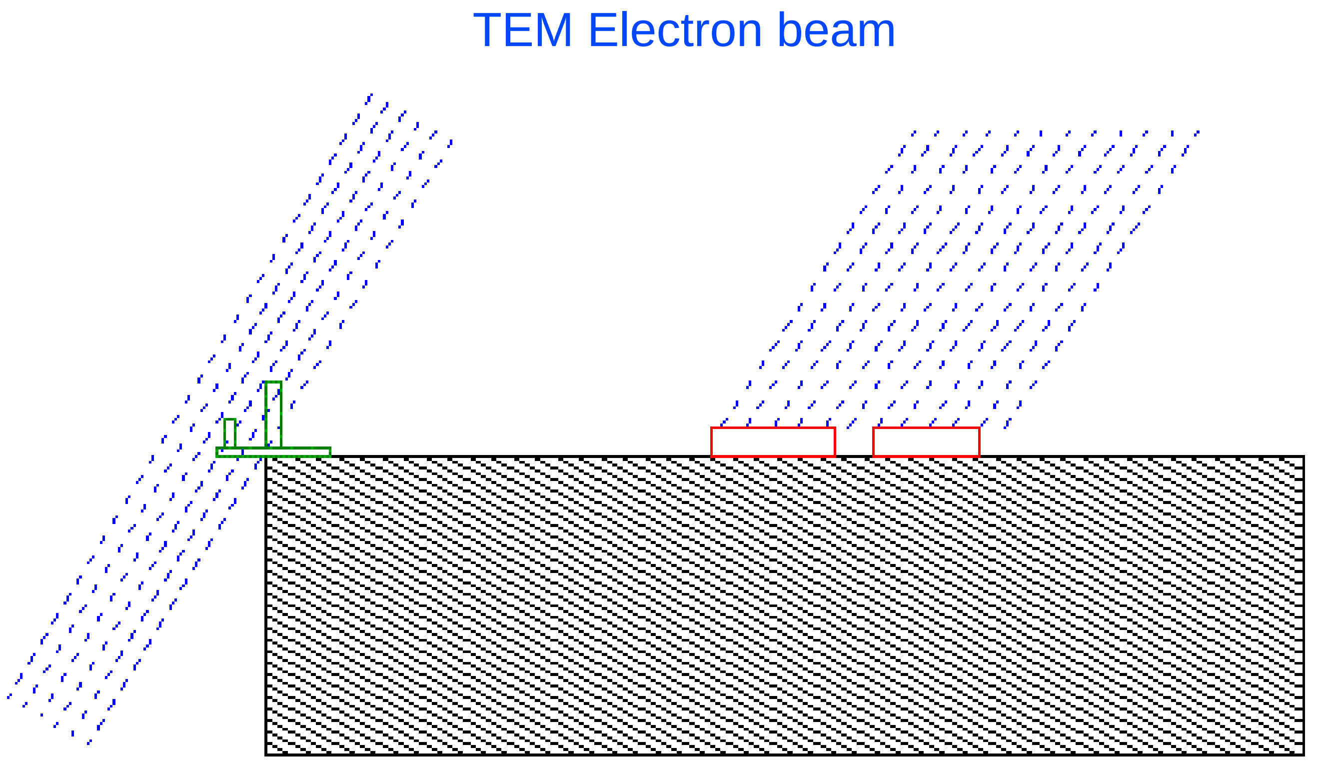
1. Origin for conduction transition ?

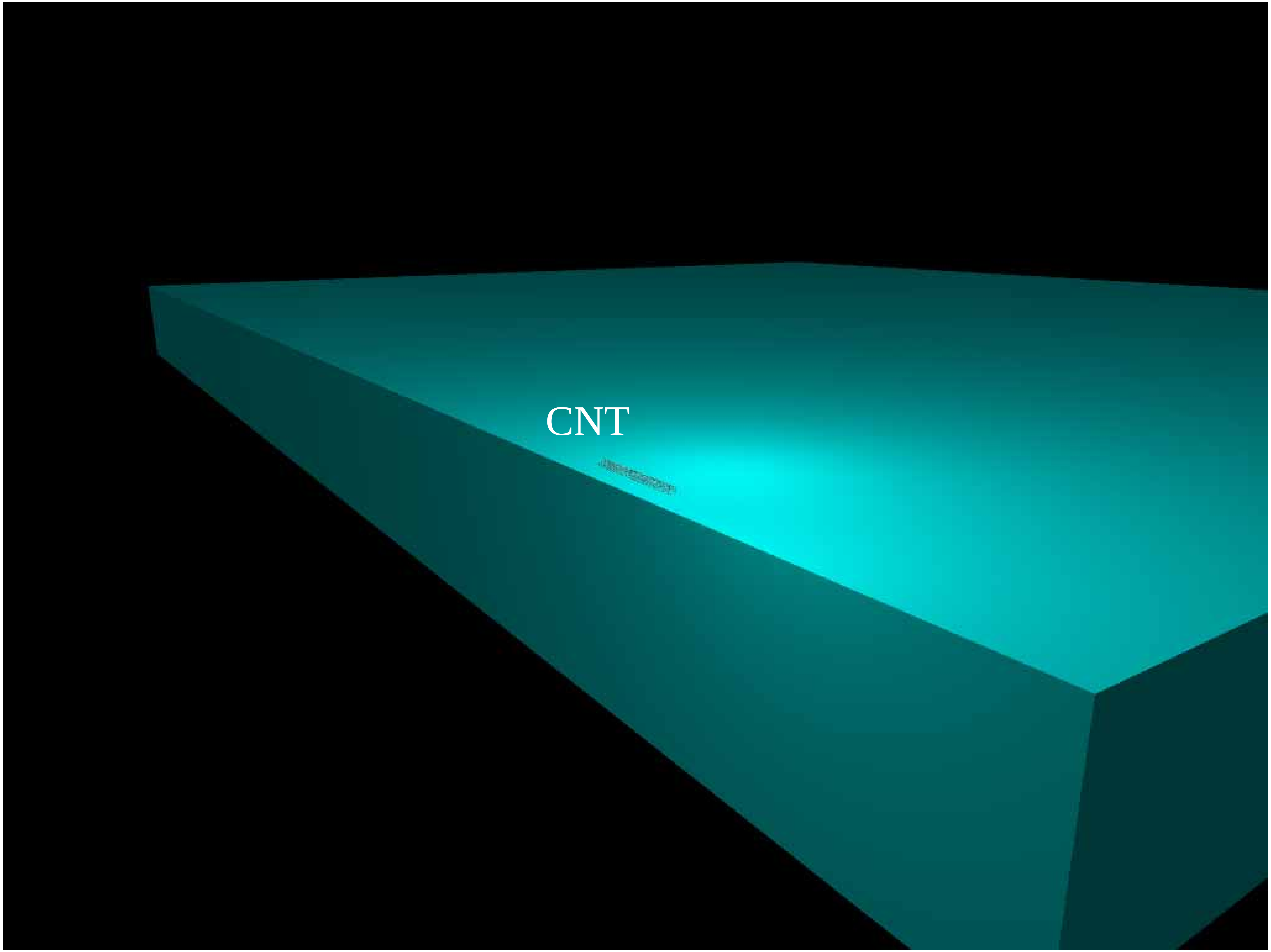
2. Filling profile ?

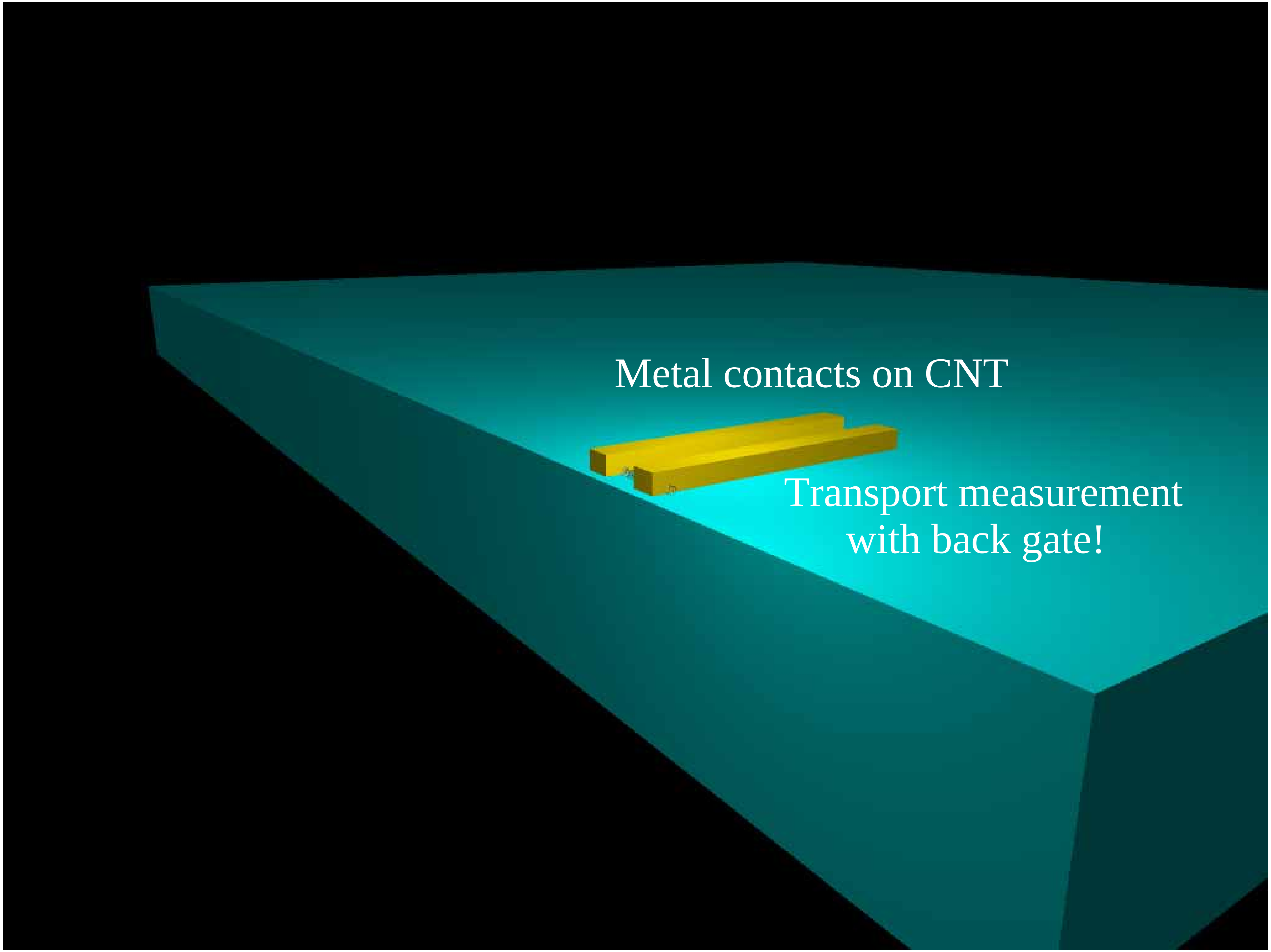
3. (n,m) = ?

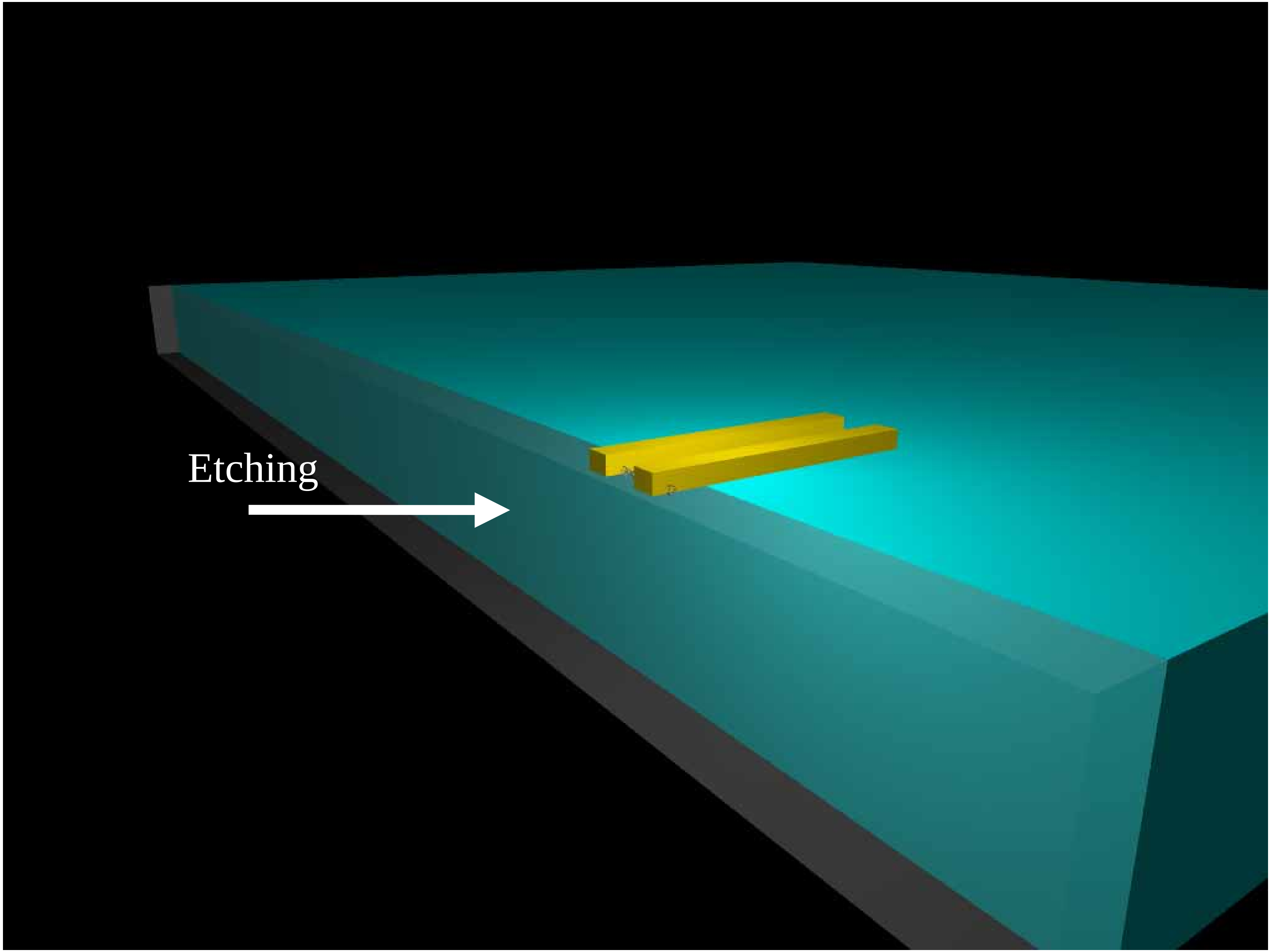
Transport + TEM

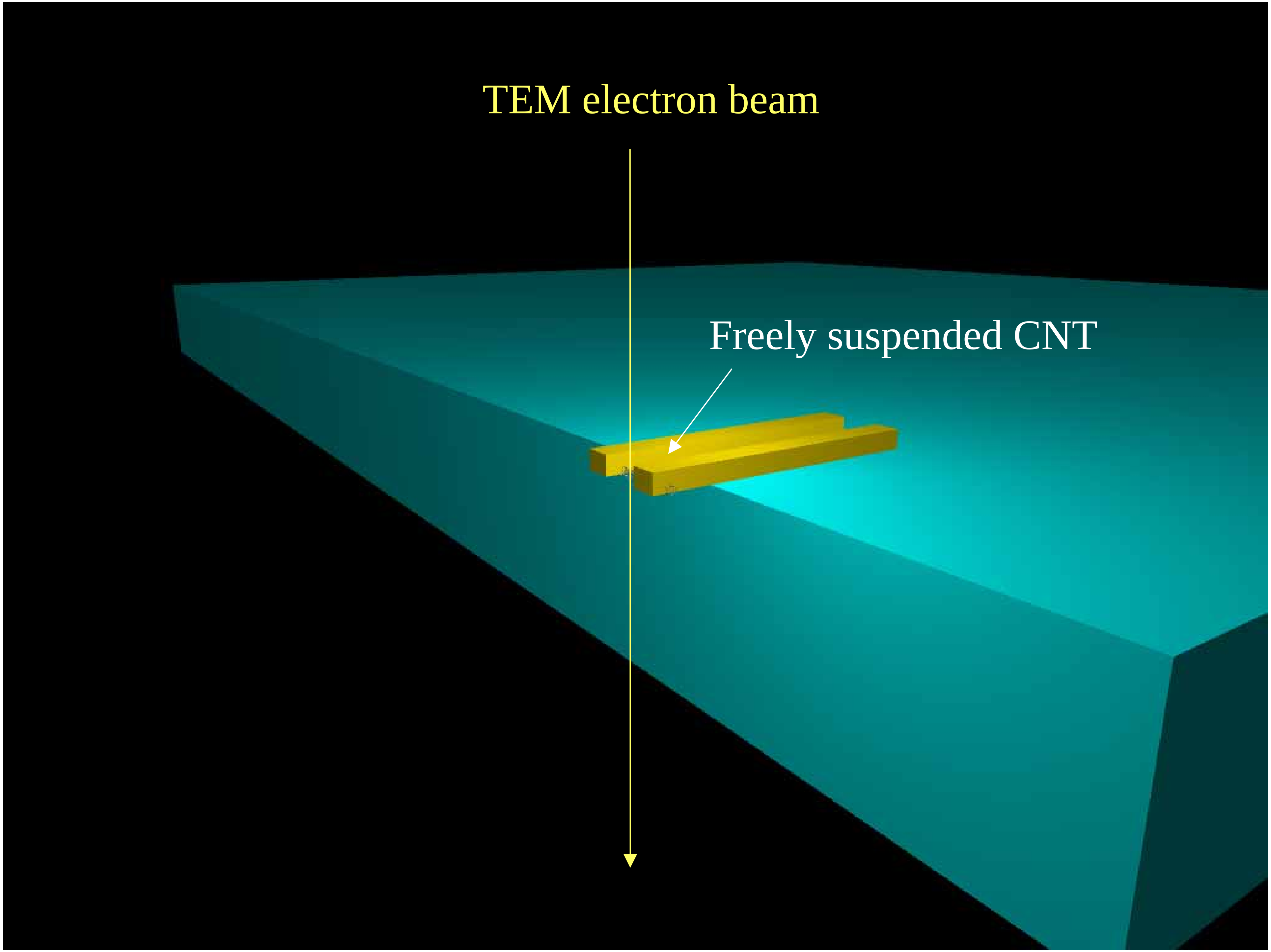
Idea: Structures on the edge of a chip

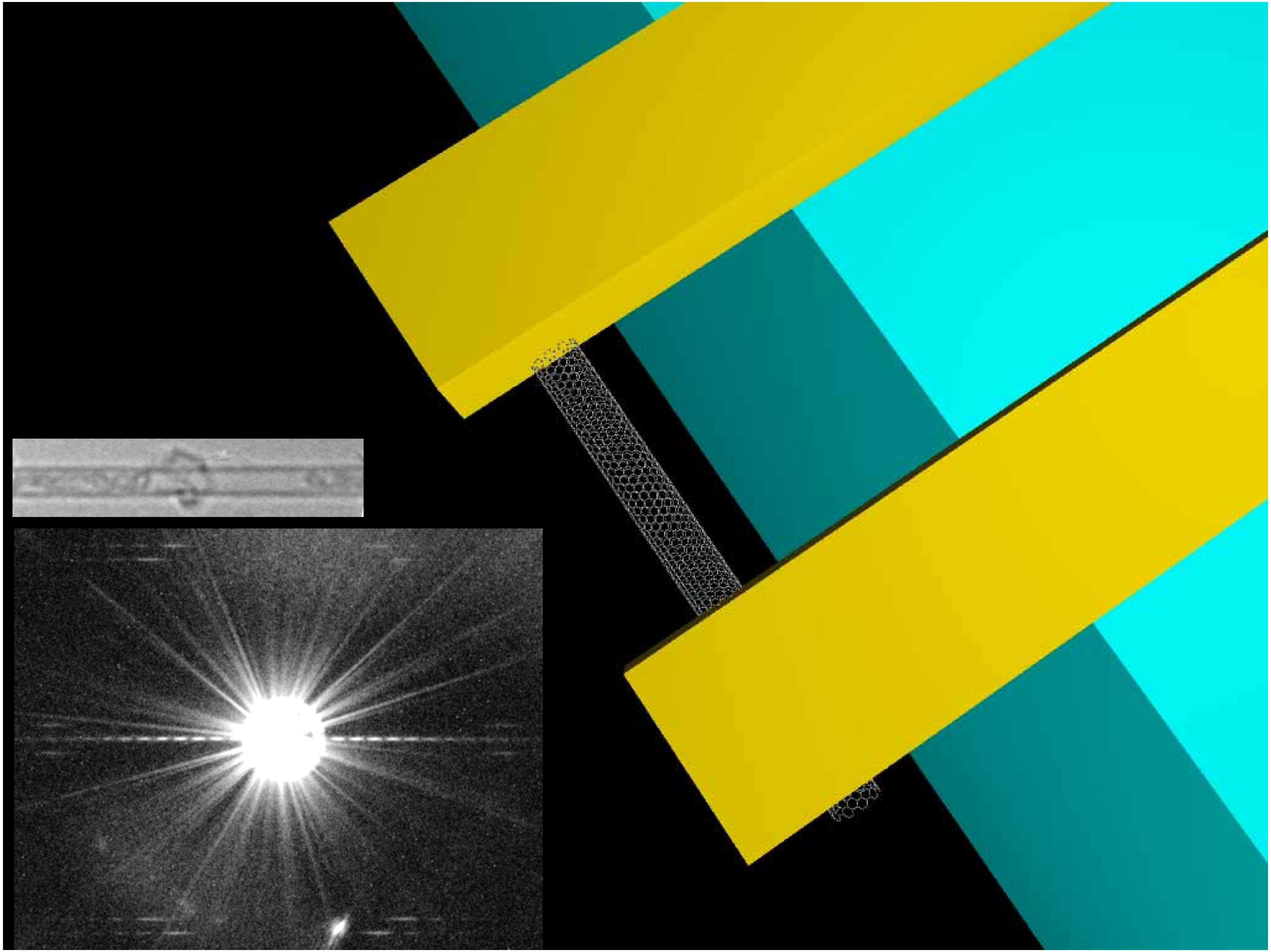



CNT

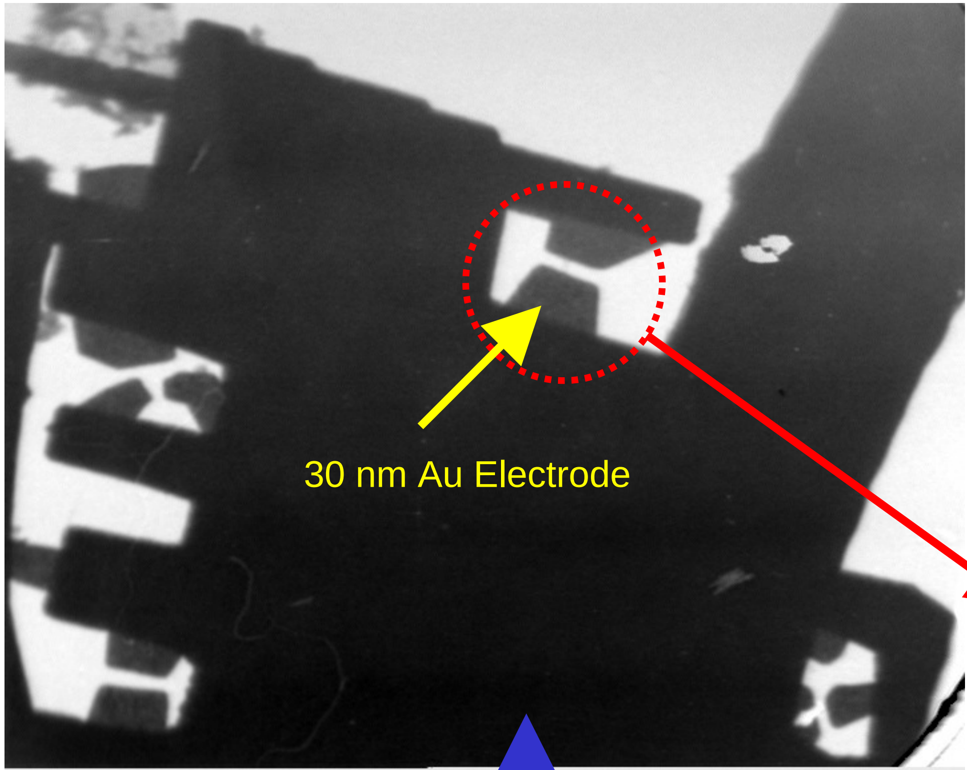

Metal contacts on CNT
Transport measurement
with back gate!


Etching


TEM electron beam
Freely suspended CNT



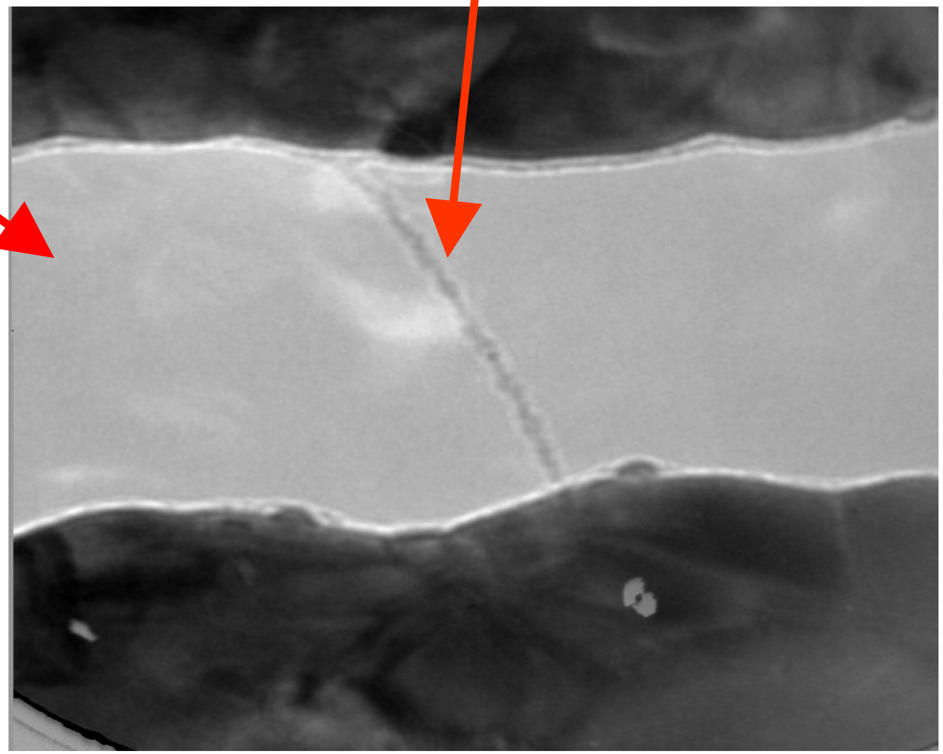
Transport + TEM



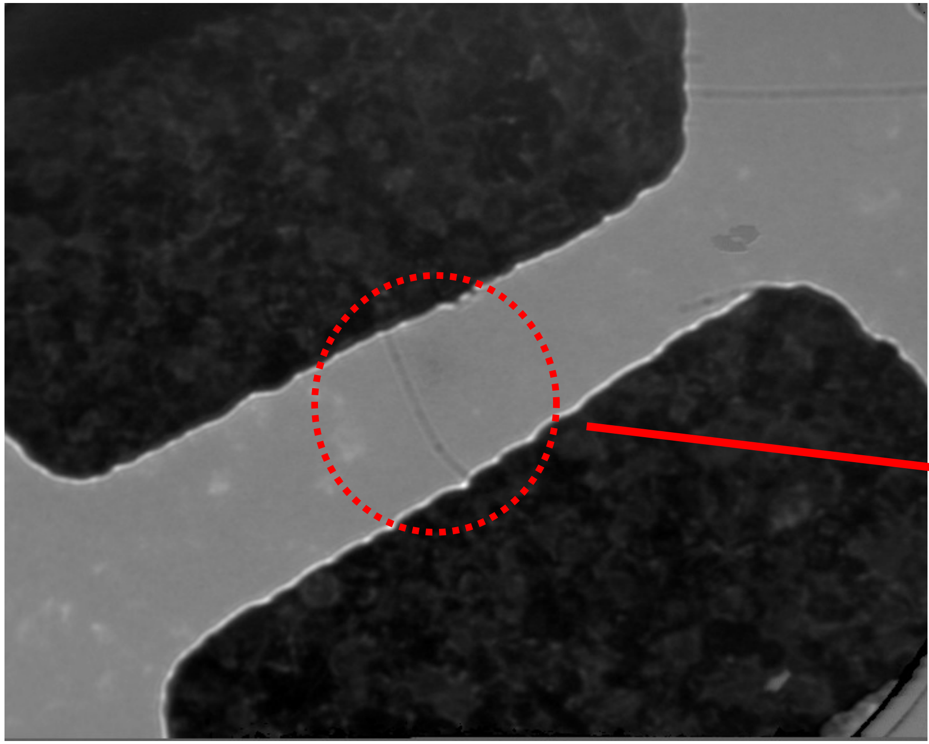
100 nm Au for mechanical support and heat dissipation, added after transport measurements

Transport were carried out on the tubes near the cleaving edge, under which the substrate was etched away for TEM observation

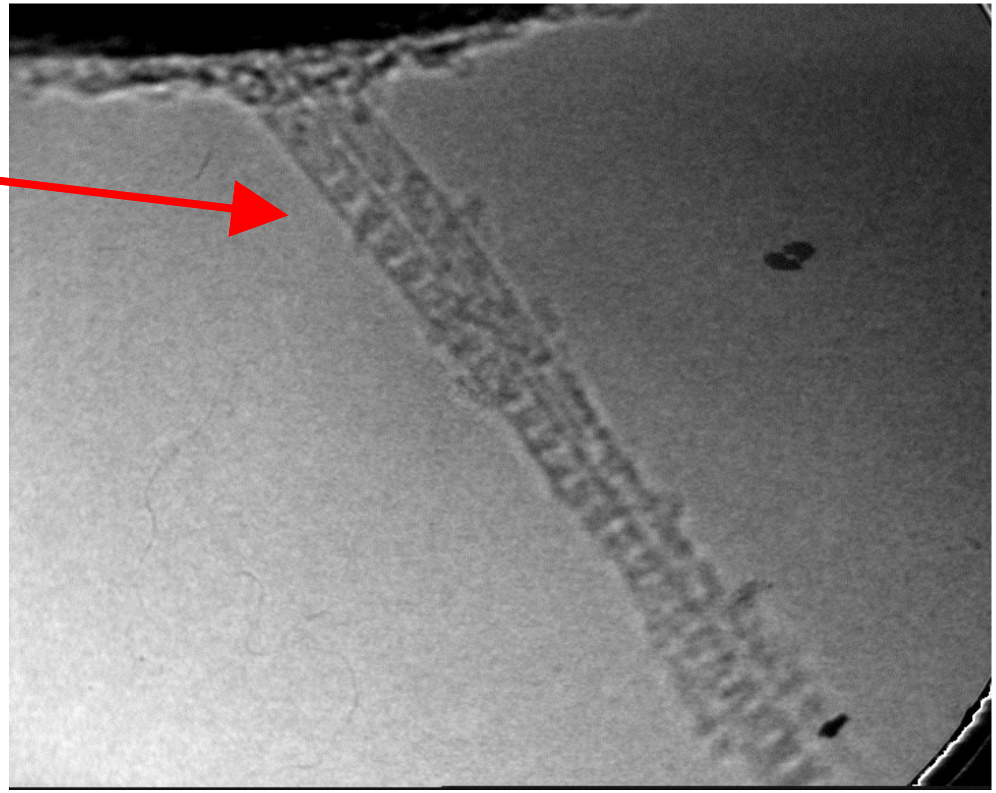
Suspended single nanotube measured in transport



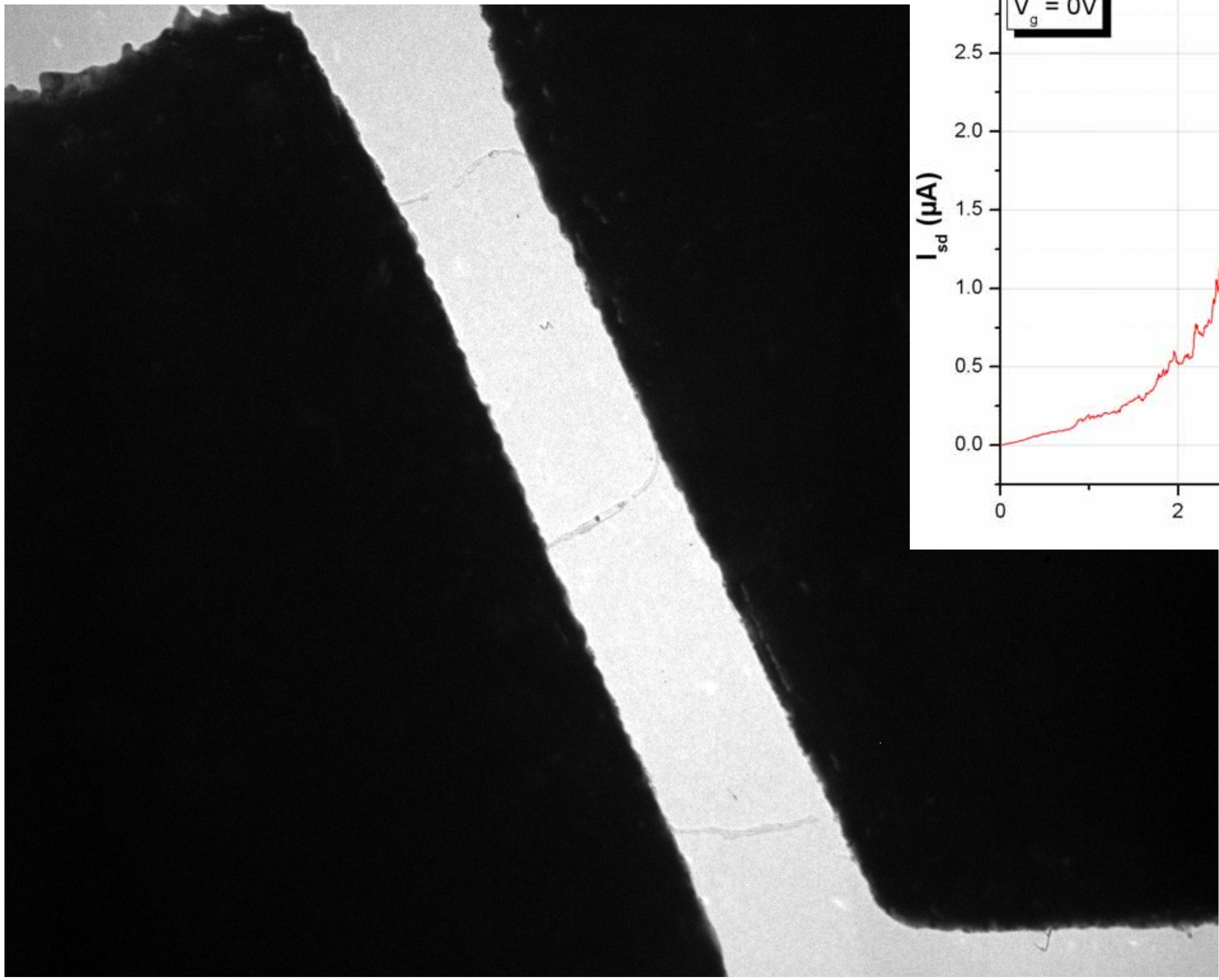
Transport + TEM

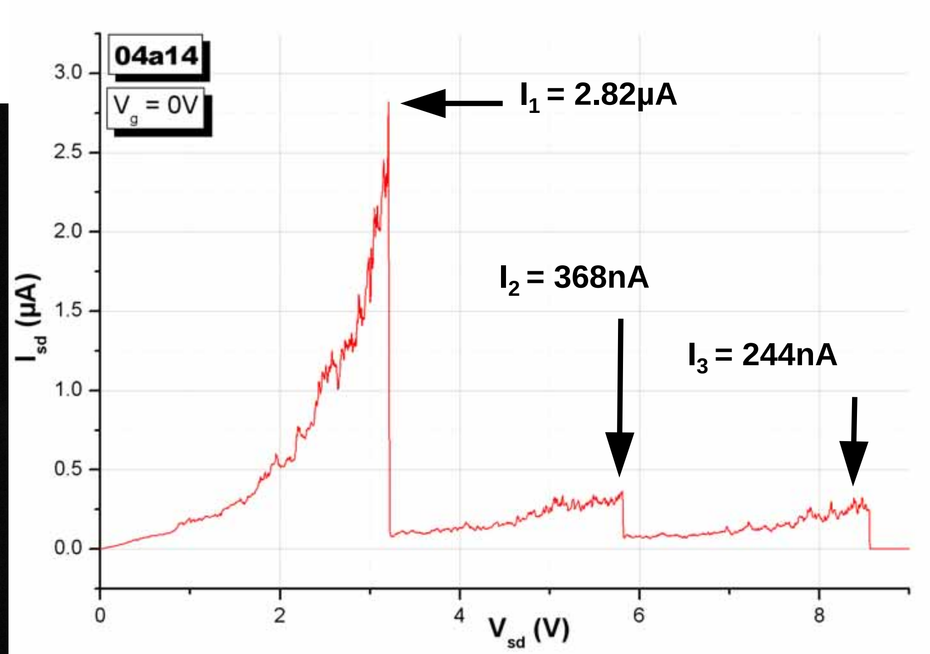


Two nanotubes, one if filled with fullerene and the other is not.



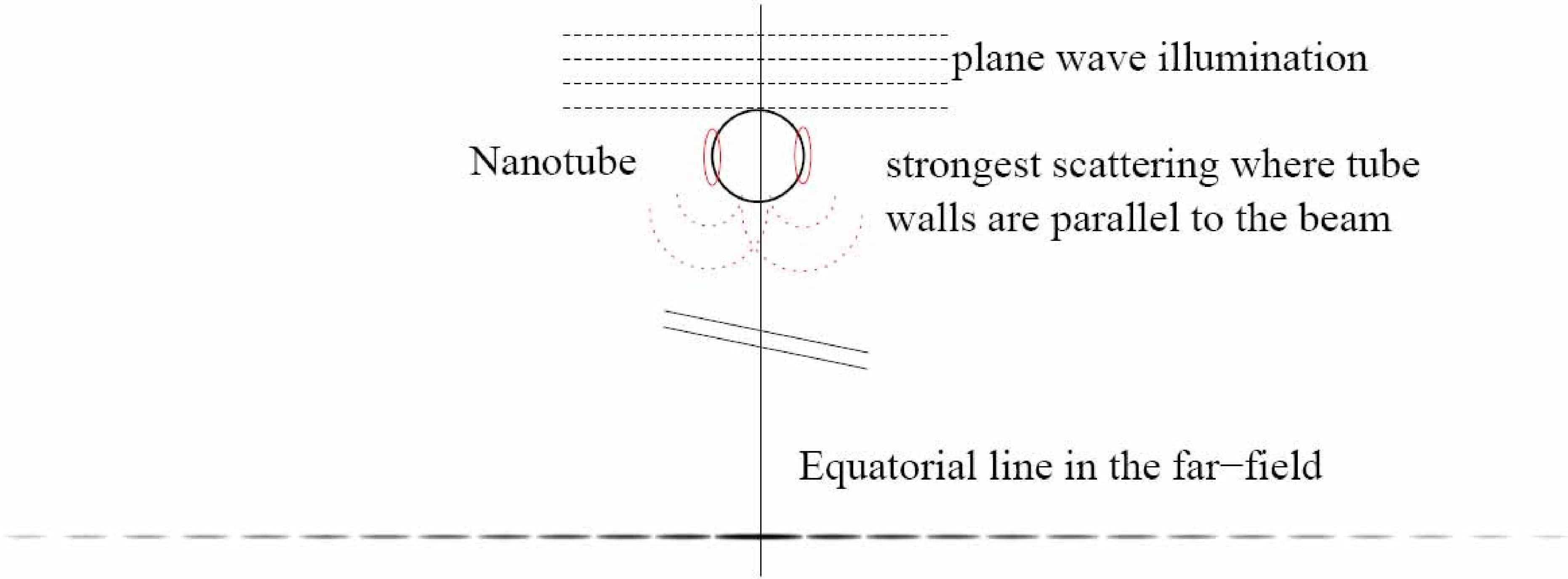
In situ transport measurement





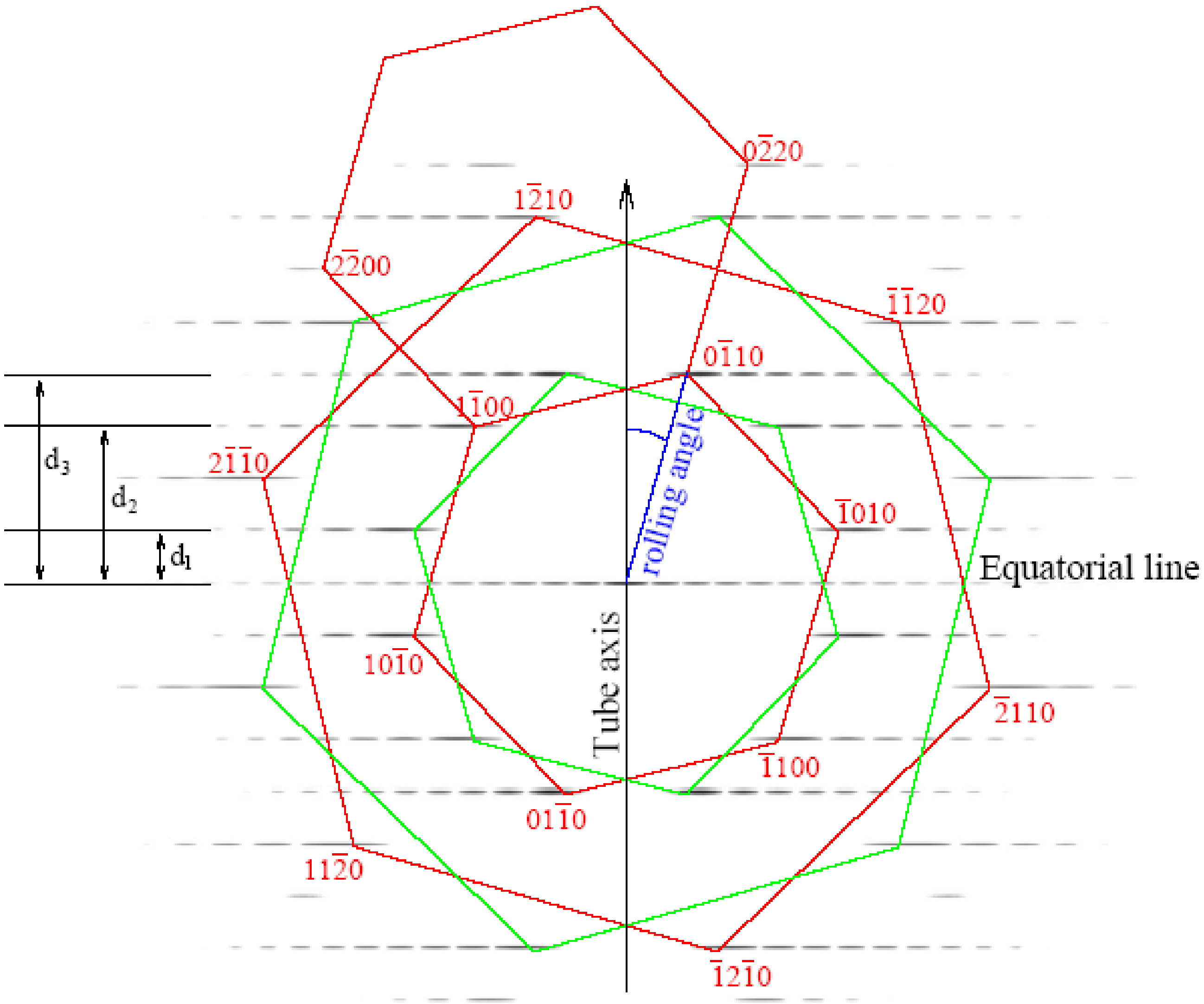
Nanotube (n,m) assignment

Determing the diameter from the periodicity of Equatorial line



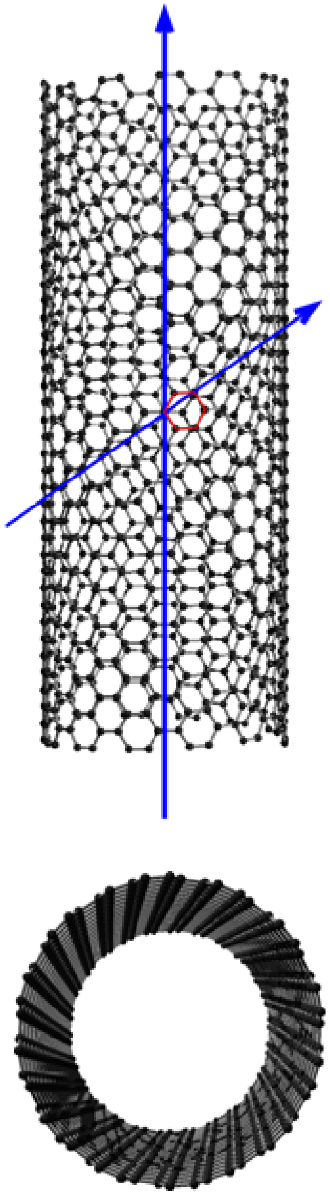
Nanotube (n,m) assignment

Determing the chiral angle from: $\arctan\left(\frac{1}{\sqrt{3}} \cdot \frac{d_2 - d_1}{d_3}\right)$

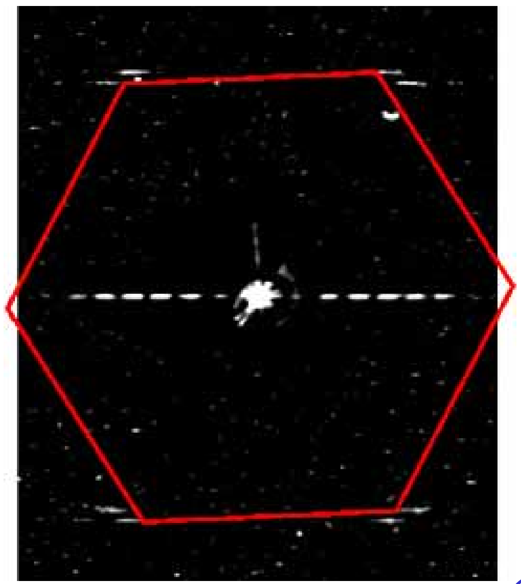


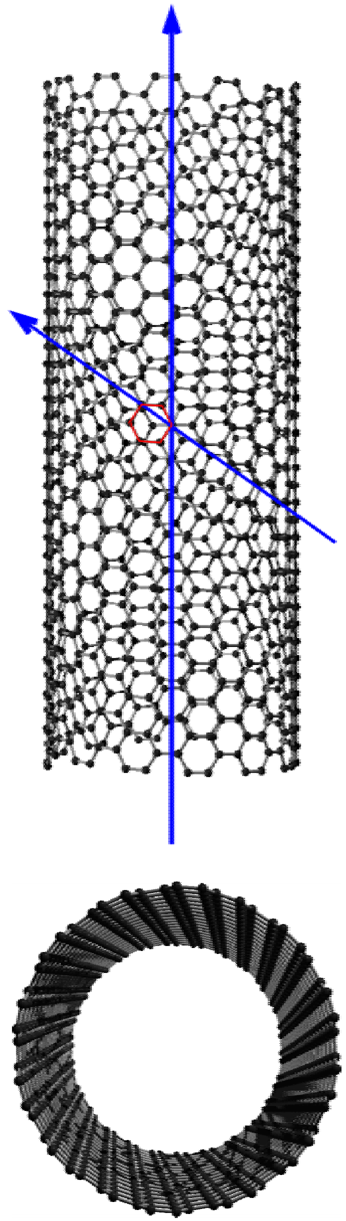
Nanotube diffraction pattern

Hexagon orientation =>
Chiral angle θ



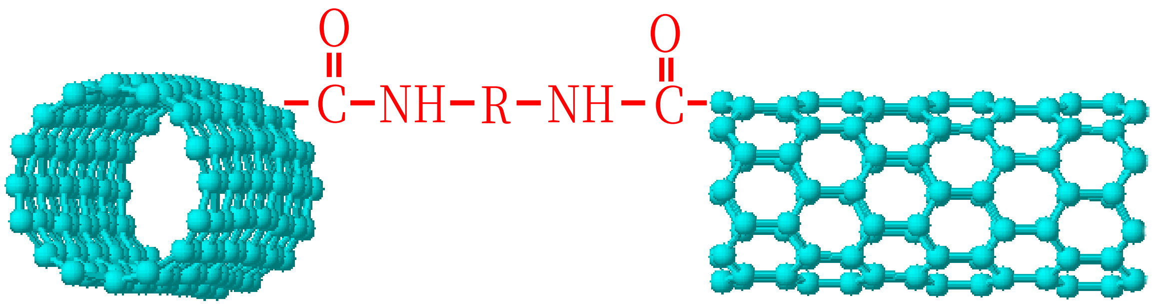
(14,12)

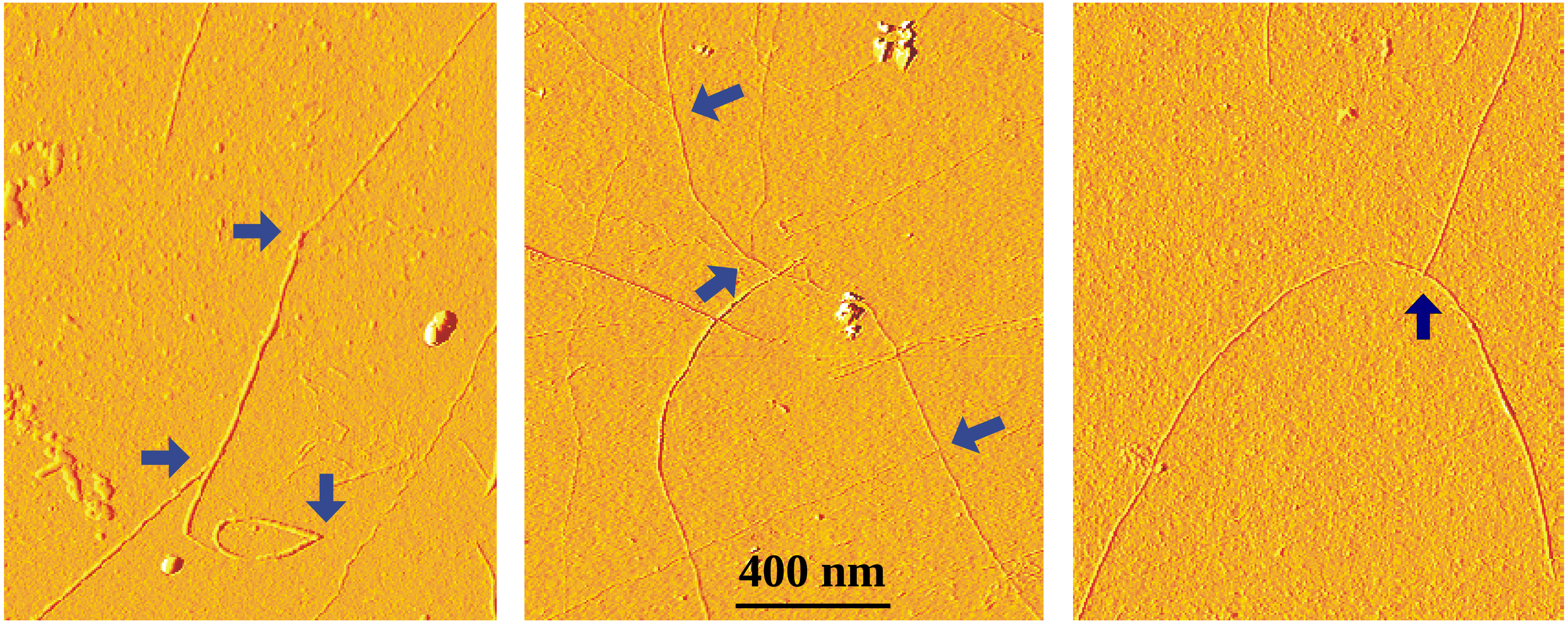




(14,-12)

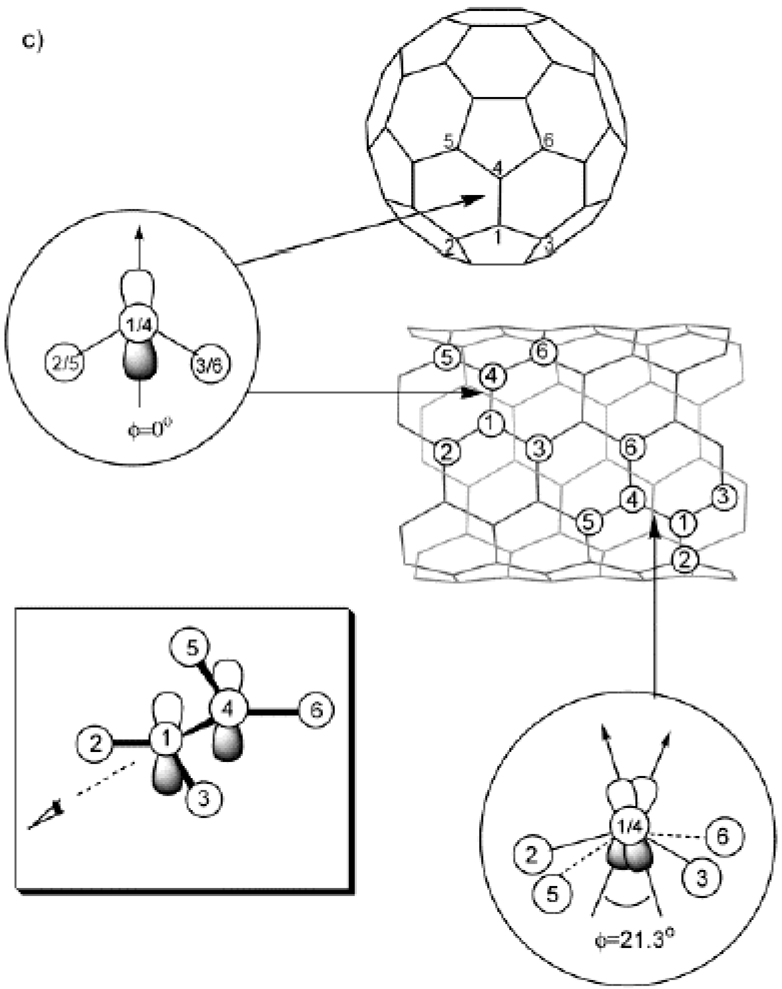
Bandgap madulation (II) – T junction





P. W. Chiu *et al*, Appl. Phys. Lett. 80, 3811 (2002).

Bandgap madulation (II) – T junction



Chemical properties

1. π orbital misalignment:
   C60 = 0
   (5,5) CNT = 21.3°

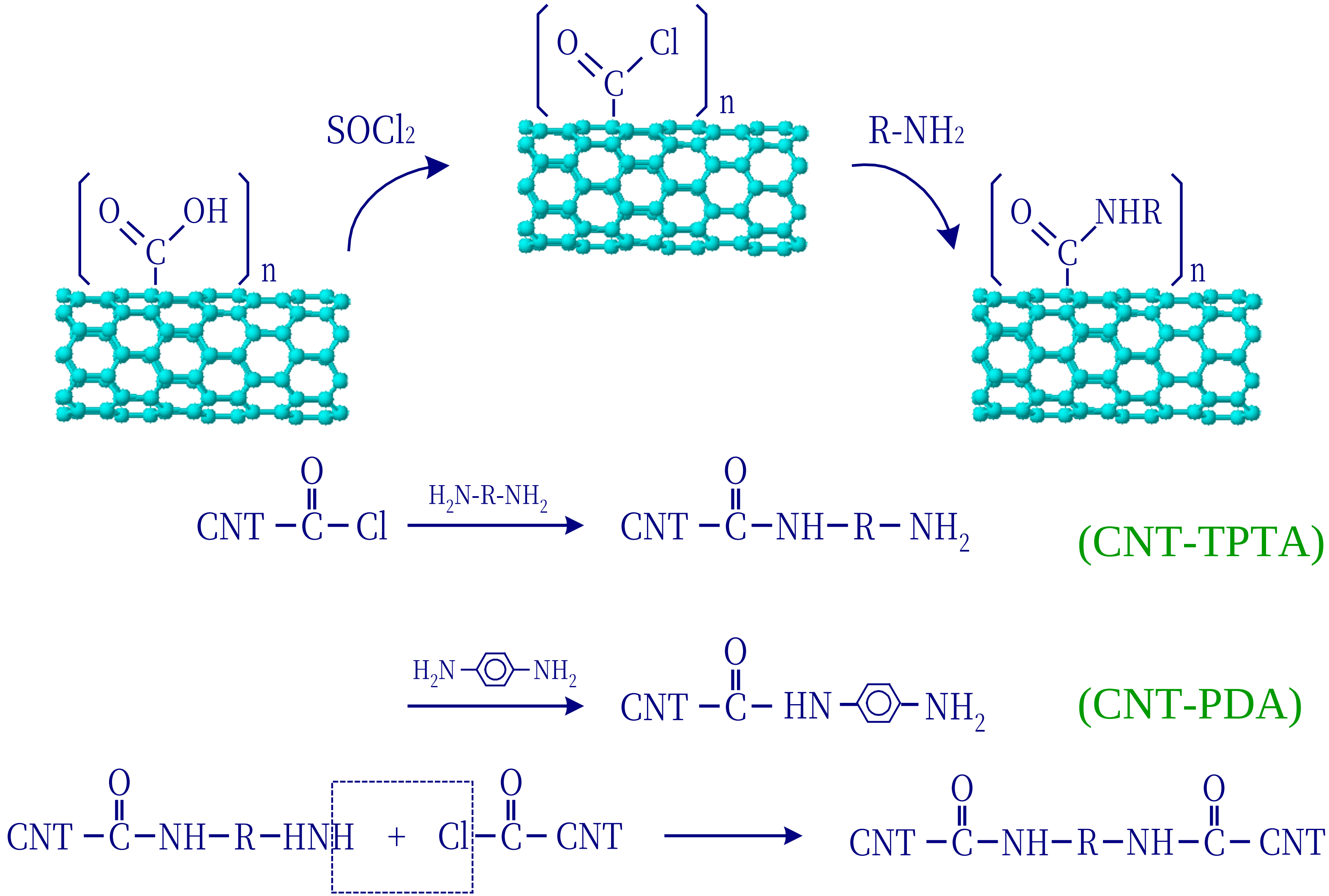
2. π orbital misalignment:
   increase with decreasing CNT diameter

3. π orbital misalignment:
   proportional to lattice strain

4. turn hydrophobic into hydrophilic
   by surface modification

Bandgap madulation (II) – T junction

Chemical functionalization

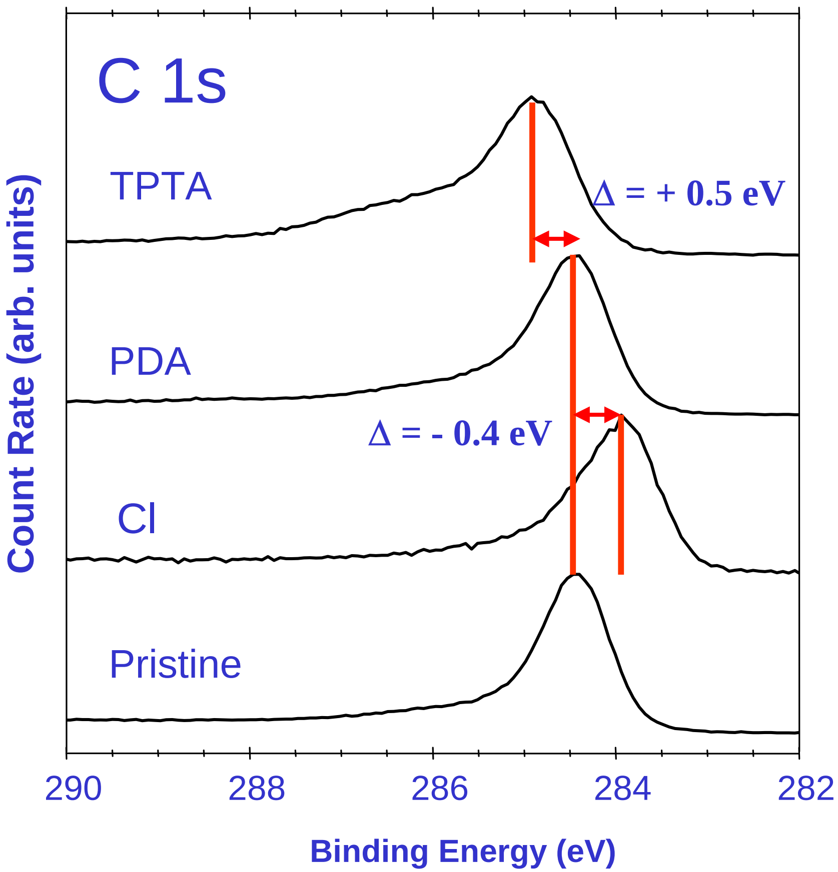


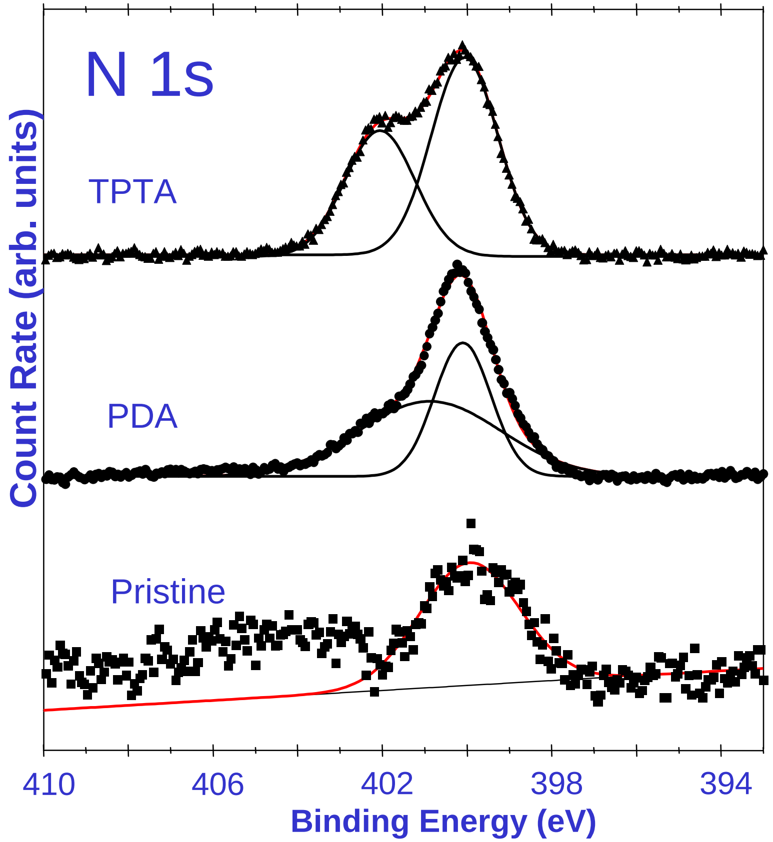
P. W. Chiu *et al*, Appl. Phys. Lett. 80, 3811 (2002).

Bandgap madulation (II) – T junction

Evidence for functional group attachments:

- Functionalization induced dopping effects
- Binding energy of diamine in XPS

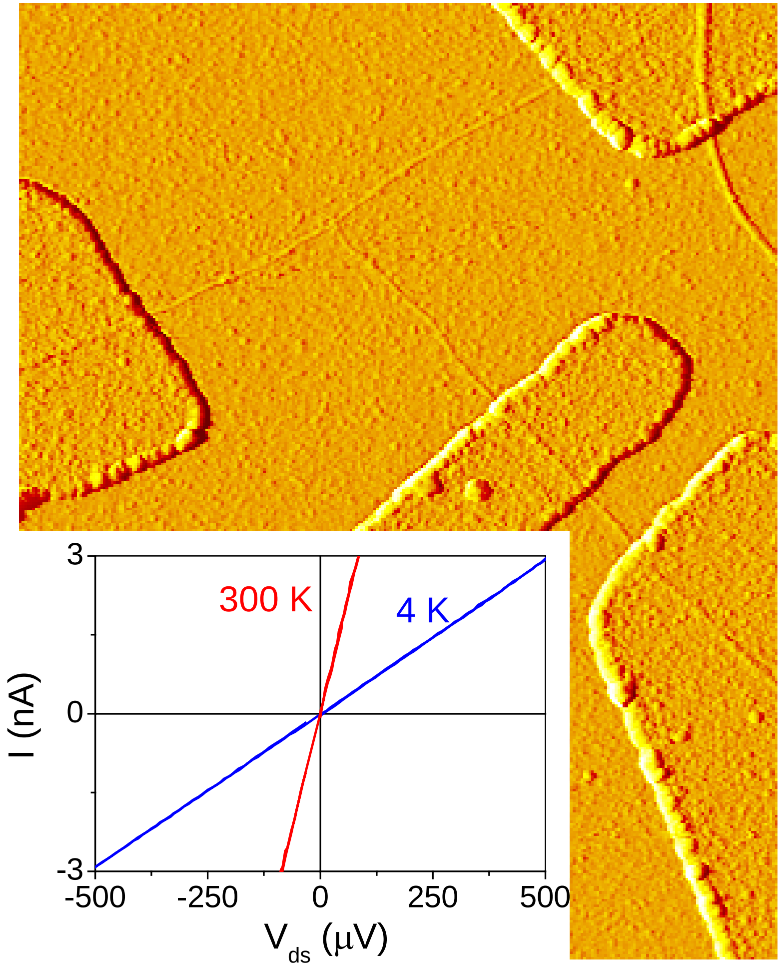




Bandgap madulation (II) – T junction

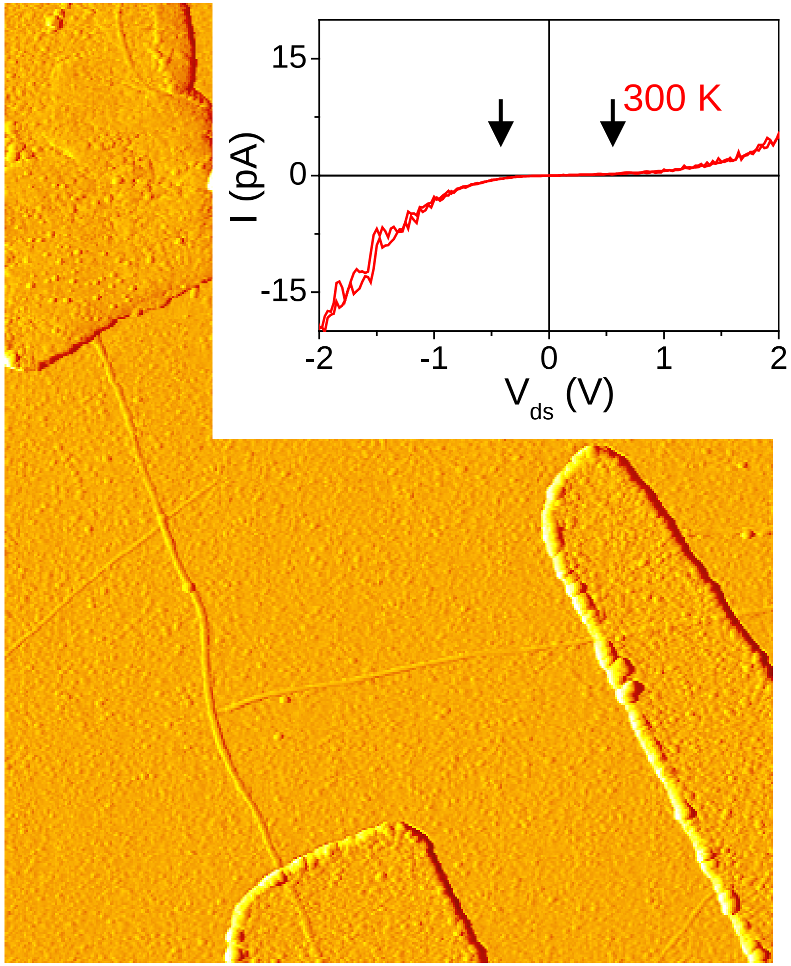
Conductive linker (PDA)

- Interconnection
- asymmetric Schottky barrier

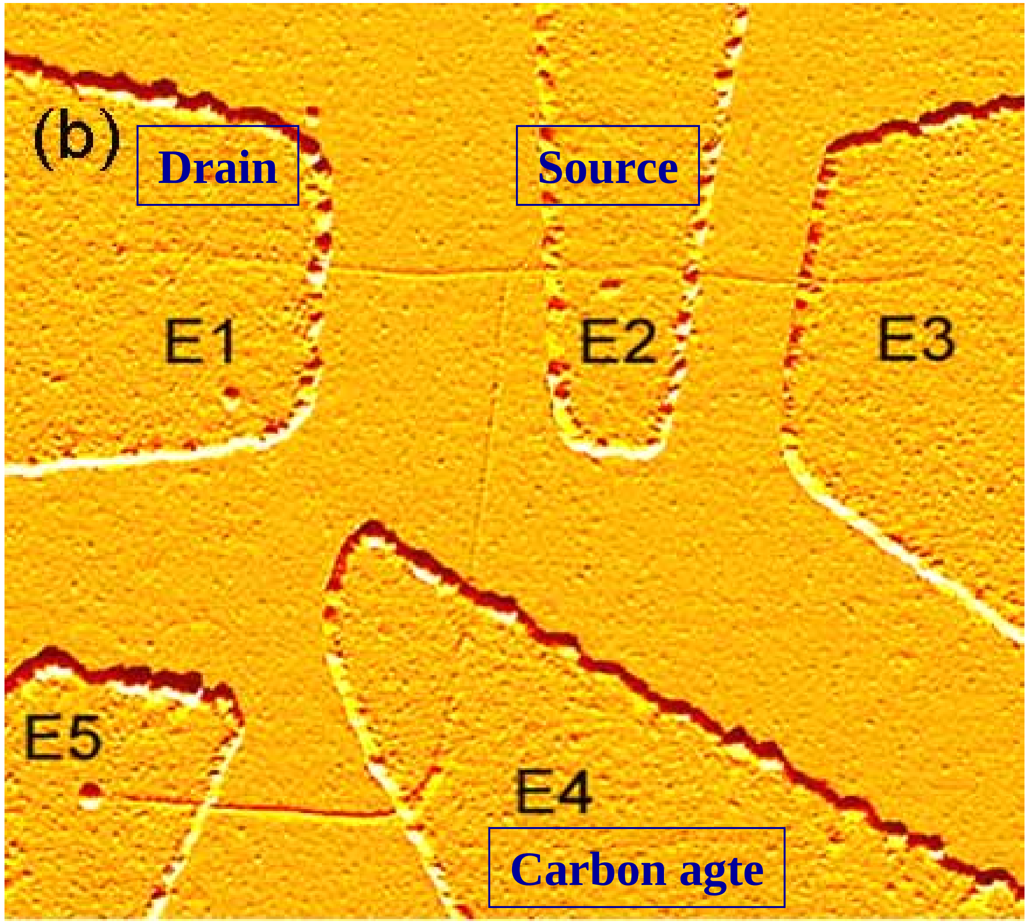


Nonconductive linker (TPTA)

- In-plane carbon gate



Bandgap madulation (II) – T junction

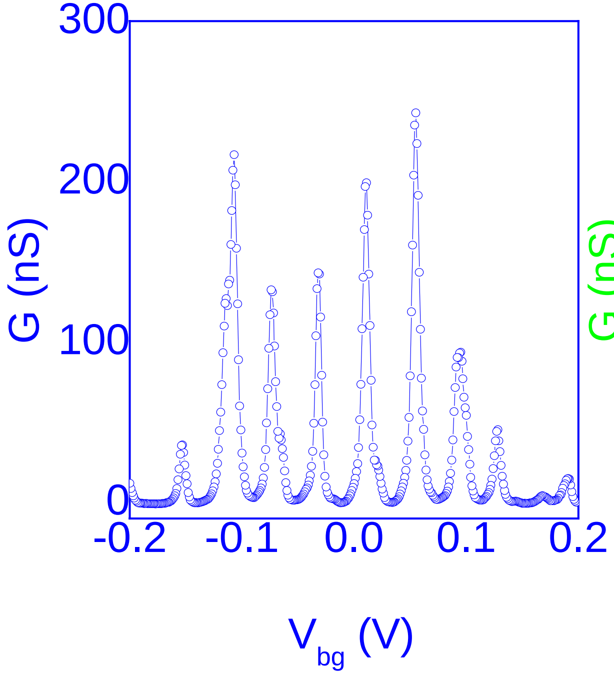


E3/E5: Diagnostic electrodes

Bandgap madulation (II) – T junction

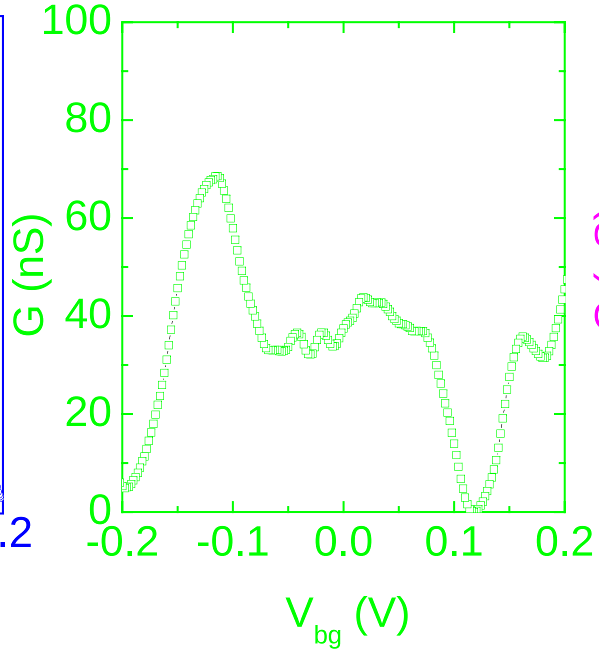
E_{cg} = 0

Single electron charging



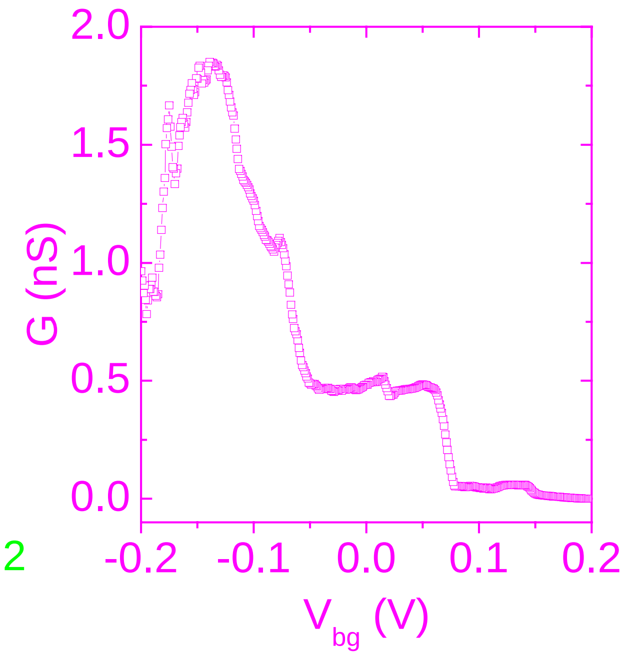
E_{cg} = + 4x10^3 V/cm

Irregular conductance oscillation



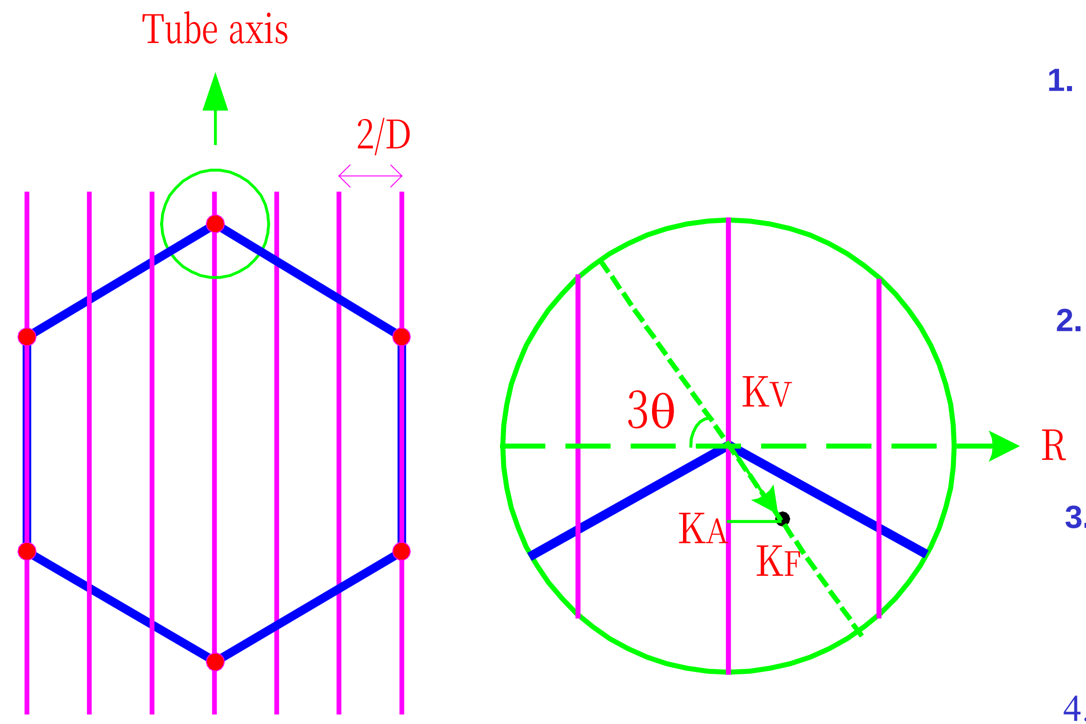
E_{cg} = + 1x10^4 V/cm

Subband population ?



P. W. Chiu *et al*, Phys. Rev. Lett. 92, 246802 (2004).

Bandgap madulation (II) – T junction

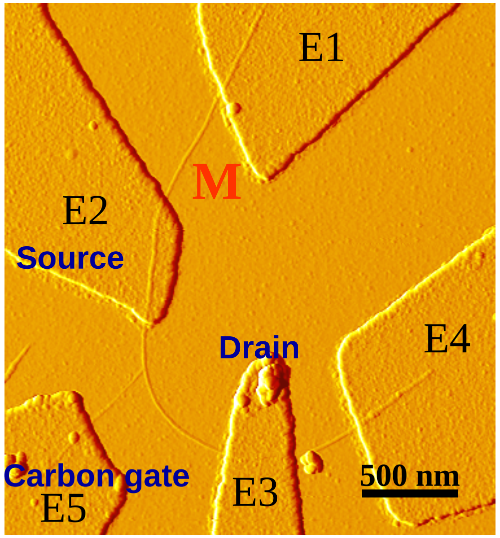


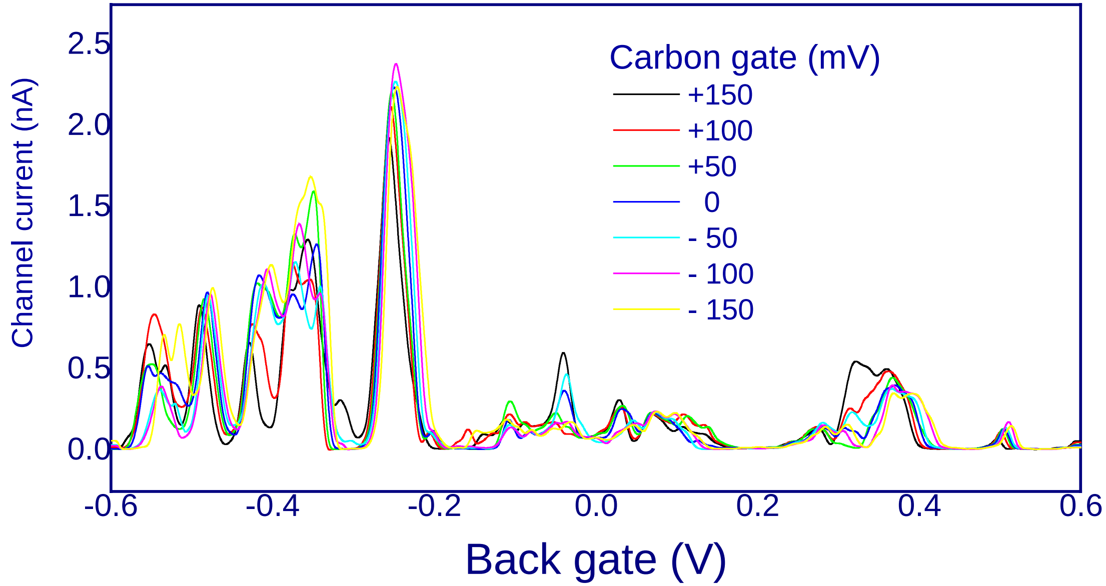
$\Delta k_{\perp} = 0$ $\Delta k_{\perp} = |k_F - k_A|$

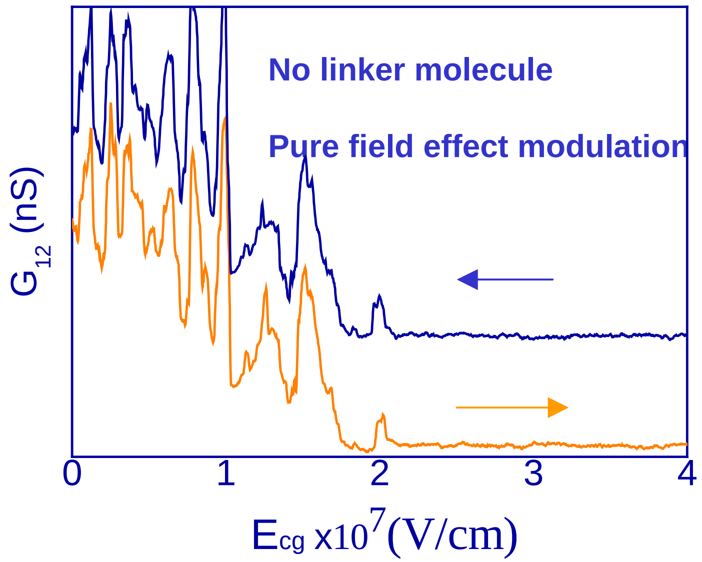
1. **Lattice expansion/contraction** ⟷
   Electromechanical actuation/ Optomechanical bending
2. **Molecular linkers** ⟷
   Nano-manipulator
3. **Mechanical force exerts on tube circumference.**
4. $\Delta k_{\perp} = 0 \longrightarrow |k_F - k_A| \propto \Delta E_g$
5. $\Delta E_g \propto |V_{pp\pi}|[(1+\nu)\sigma\cos 3\theta + \gamma \sin 3\theta]$

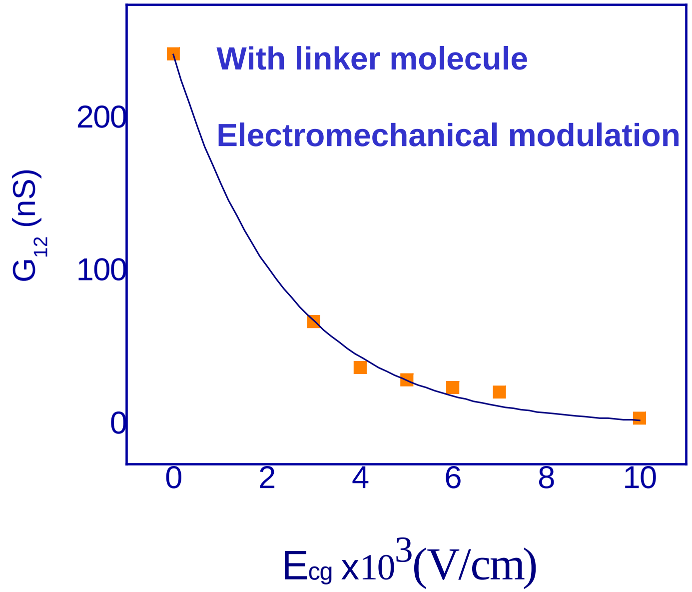
L. Yang, and J. Han, Phys. Rev. Lett. 85, 154 (2000).

Bandgap madulation (II) – T junction









Summary

1. Manipulating band strucure

- ★ Nanotue peapods
- ★ Nanotube T junctions

2. Determinating band structure

- ★ TEM on the same nanotube
- ★ Determining diameter and chiral angle
- ★ (n,m) assignment

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